CARBON CATALYSTS FROM COAL FOR ENVIRONMENTALLY RELEVANT REACTIONS

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INTRODUCTION

Activated carbons can be produced from coals by a variety of thermal and chemical-thermal methods. A method related to the present paper is the chemical treatment of coal with aqueous KOH first at relatively low temperature (315-482 °C), followed by carbonization at higher temperatures in the range of 704-982 °C (1). In previous publications (2-4) we have shown that temperatures as low as 75 °C in the first step, followed by carbonization at 600-900 °C gave good quality, high surface area, active carbons.

Activated commercial carbons produced from coal are used for water purification, solvent recovery, supports for catalysts (5) and for SOx and NOx removal from gas streams (6).

Another important use of carbon catalysts for environmental cleaning is the removal of halogen from halogen-containing compounds. Two basic approaches could be used: 1. gas phase catalyzed oxidation of the halogen-containing compounds to carbon dioxide and the corresponding halogen-containing acid (7) and 2. catalytic dehalogenation. The case of carbon catalyzed dehalogenation of an alkyl chloride was studied in detail by Sohr and Boehm (8). The case of liquid-phase carbon black catalyzed hydrodehalogenation of halogenated aromatic compounds was studied by Farcasiu et. al (9,10). An important difference between the oxidative dehalogenation and hydrodehalogenation is that in the oxidative method the carbon in the halogen-containing compounds is transformed into carbon dioxide, while in hydrodehalogenation the halogen removal from an aromatic hydrocarbon is selective and the hydrocarbon skeleton is maintained. The two methods address two different environmental situations, i.e. the removal of a high concentration contaminant (oxidation), or the selective removal of halogen from a hydrocarbon mixture containing some halogen compounds.

The use of carbon materials such as some carbon blacks, for hydrodehalogenation and hydrodehydroxylation of condensed polyaromatic compounds has been reported (9,10). Very good activities and selectivities have been observed with some carbon blacks for the hydrodehalogenation of halogenated condensed polyaromatic compounds such as halogenated naphthalenes, phenanthrenes, and pyrenes. Only very modest dehalogenation was observed for compounds, such as 4-chlorobiphenyl, containing halogen substituted at benzenic rings.

When carbon materials are used as catalysts for specific reactions, the preparation of the carbon material could be customized to substantially increase in the catalytic activity. The role of the carbonization temperature on the catalytic activity (for hydrocracking of alkyl substituted condensed polyaromatics) of resorcinol-formaldehyde aerogel-based materials has been reported (11). In that work it was shown that the catalytic activity of the carbonized aerogels increases with the carbonization temperature, reaches a maximum around 1050 °C and then decreases dramatically. Graphite is not active catalytically in such hydrocracking reactions.

We have found that under very defined preparation conditions, carbon materials prepared from coal could be very active hydrocracking and hydrodehalogenation catalysts for aromatic compounds. We reported recently (12) the influence of the method of preparation on the catalytic activity of coal-derived carbon catalysts for hydrocracking and hydrodehydroxylation reactions.

In the present publication, we will discuss how various parameters could be varied during

the preparation of coal-based catalysts to optimize their activity for the dehalogenation reaction of halogenated aromatic compounds.

EXPERIMENTAL

Various coals were activated using a two step procedure at the Center for Applied Energy Research (2). The first step involved the mixing of a solution of potassium hydroxide with -100 mesh cleaned coal (KOH to coal weight ratio 1.42:1). This mixture was heated at 75 °C for two hours under nitrogen. The heat treatment temperature (HTT) at 800 °C or 900 °C for one hour is the second step, followed by leaching to remove KOH.

Indiana VII is a hvC bituminous coal and was cleaned at Entech Global, Inc, using two different methods. Selective agglomeration (SA) is a method for rejecting mineral impurities from ground coal using pentane and heptane as reusable bridging liquids. Microcel™ Column (MC) is a column flotation method. Wyodak Black Thunder is a subbituminous coal, and Illinois Basin hvC coal (IBC) is a high volatile, bituminous coal.

The surface areas of these activated carbons were measured by nitrogen adsorption at 77 K using the BET method.

Two activated carbons, WS 4 and Centaur™ HSV, were donated by Calgon Carbon Corporation. The WS 4 carbon is prepared from dense wood and thermally activated, while Centaur™ HSV is prepared from bituminous coal. A carbon black, Black Pearls 2000 (BP2000), was donated by Cabot Corporation.

The dehalogenation activity of various carbon catalysts was tested for the debromination of 1-bromonaphthalene in the presence of a hydrogen donor, 9,10-dihydrophenanthrene (9,10-DHP). The reaction conditions were in all cases: 350 °C, 1 hour, wt. ratio 1-bromonaphthalene : 9,10-DHP : catalyst 1 : 4 : 0.1. The experimental procedure is explained elsewhere (9).

Gas chromatographic analysis of the product was carried out on a Hewlett Packard 5890A Series II, equipped with a JW-SE-42 column and a FID.

RESULTS AND DISCUSSION

We observed previously (9,12) that the reaction-specific catalytic activity of some synthesized carbon catalysts could be optimized by varying the preparation conditions. We observed that the preparation is reaction-specific and chemical reactions with various mechanisms could require quite different carbon materials to achieve optimum catalytic activity. We believe this fact is related to the presence of several types of active sites on the surface of the catalyst and to their relative concentration and/or strength, as a function of the preparation conditions. We will discuss how such a preparation could be optimized for the dehalogenation of halogenated condensed polyaromatic hydrocarbons. The method for the synthesis of coal-based carbon catalysts is described in the experimental part. Several parameters are very important in the preparation of coal based catalysts according to this method:

1. the temperature of step 2 (HTT)
2. the rank of coal
3. the method of coal preparation/cleaning prior to activation

1. Influence of the temperature in step 2 (HTT)

We have found that catalysts for hydrodebromination and hydrodehydroxylation reactions can be made by chemically activating coals (Table 1). These activated carbons perform better than commercially available carbon materials such as BP2000 (Cabot), WS 4 and Centaur™ HSV (Calgon). As shown in Table 1, the extent of the hydrodebromination of 1-bromonaphthalene is greatest when the heat treatment temperature (HTT) in step 2 reaches 800 °C. At this temperature, surface area is at a maximum, but as can be observed from the conversion data, the increase in surface area alone cannot explain the difference in reactivity. In the case of the hydrodehydroxylation of 2-naphthol, the maximum conversion is reached at 700 °C and appears to become steady above that temperature. For comparison we show data (Table 1) on the catalytic activity of some commercial active carbons. BP2000 and WS 4 are nearly the same for both reactions. However taking into account the higher surface area of BP2000, WS 4 appears to be a

slightly more active catalyst. Centaur™ HSV, which is made from bituminous coal, is the least active in our reactions.

The products in the hydrodebromination reaction are tetralin, naphthalene, and 2-bromo-5,6,7,8-tetrahydronaphthalene. The hydrodehydroxylation reaction yields tetralin, naphthalene, naphthalone, and 2-hydroxy-5,6,7,8-tetrahydronaphthalene.

The influence of HTT in step 2, was also observed for Indiana VII activated carbons in Table 2.

2. Influence of coal rank

We found that a HTT of 900 °C is optimal for both Indiana VII bituminous coal and Black Thunder subbituminous coal in the hydrodehalogenation of 1-bromonaphthalene. However, if we compare the highest hydrodehalogenation values, the catalyst prepared from subbituminous coal is better than the catalyst prepared from bituminous coal. Under our test conditions, the best catalyst obtained from Indiana VII gave a conversion of 1-bromonaphthalene of 62% as compared with 76% for the best preparation from Black Thunder subbituminous coal. Whether these results represent the general case, and better catalysts for the debromination can be obtained from subbituminous coals, is far from being proven and therefore more cases should be studied.

3. Influence of the method of coal cleaning on the catalytic activity of the carbon catalysts

To avoid a large concentration of mineral matter in the activated carbons prepared from coals, the coal mineral matter should be substantially removed prior to activation. We started a systematic study in this area using Indiana VII precleaned by Entech to about 2.6 % ash by two different cleaning methods: solvent agglomeration and column flotation (see the experimental section). Cleaning the same coal using a dry separation method (tribo-electrostatic separation) is in progress, and the coal obtained by this method will be also used to prepare carbon catalysts. The results obtained to date are given in Table 2.

The data (Table 2) seem to indicate that coal cleaning by aqueous flotation (MC) in the presence of low amounts of surfactants is a preferred method to clean coals prior to synthesis of the catalysts. It may be that the coal cleaning method influences the types of active sites present on the surface of carbon catalysts, and therefore it may be possible to control the selective catalytic properties by choosing the conditions of the catalyst preparation.

CONCLUSIONS

Carbon materials prepared from coals could be used as active and selective catalysts for reactions of interest in environmental chemistry, such as the dehalogenation of halogenated condensed polyaromatics and the dehydroxylation of phenols or condensed polyaromatics. We have identified three important parameters to be considered in the catalyst preparation: 1. the temperature of step 2 (HTT); 2. the rank of coal; 3. the method of coal preparation/cleaning prior to activation.

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DISCLAIMER

Reference in the paper to any specific commercial product, process, or service is to

facilitate understanding and does not necessarily imply its endorsement by the United States Department of Energy.

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Table 1. Effect of Heat Treatment Temperature (HTT) on Hydrodehalogenation and Hydrodebromination Reactions.

CATALYST	HTT °C	SURFACE AREA m^2/g	% CONVERSION[1.] 1-Br-naphthalene	2-Naphthol
IL #6 IBC 106	600	835	26	35
IL #6 IBC 106	700	1081	40	48
IL #6 IBC 106	800	1583	72	48
BP-2000	-----	1475	25	36
WS4	-----	1300	22	34
CENTAUR™ HSV	-----	-----	8	20

1. Wt ratio Catalyst:1-Br-naphthalene or 2-naphthol:9,10-DHP=1:10:40; reaction temperatures for 1-Br-naphthalene or 2-naphthol are 350 °C and 410 °C, respectively , for 1 hour.

Table 2. Effects of Coal Cleaning Methods on the Conversion of 1-Br-naphthalene.

COAL[1.]	HTT °C	SURFACE AREA m^2/g	% CONVERSION[2.]
Indiana VII-SA	800	1602	50
Indiana VII-SA	900	2180	59
Indiana VII-MC	800	1790	57
Indiana VII-MC	900	1997	69

1. SA=Selective Agglomeration; MC=Microcel™ Column.
2. Catalyst:1-Bromonaphthalene:9,10-DHP = 1:10:40 at 350 °C for 1 hour.

THE POTENTIAL FOR INCREASING THE USE OF CATALYTIC CARBONS IN COMMERCIAL APPLICATIONS

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ABSTRACT

A carbon catalyst, prepared either by oxidizing activated carbon with air at 500-700°C or by oxidizing activated carbon with boiling nitric acid followed by heating it to 500-700°C, is the subject of this paper. This catalyst, designated $OAC_{500\text{-}700}$, catalyzes the removal of hydrogen chloride from alkyl halides. Because $OAC_{500\text{-}700}$ retains adsorptive properties of an activated carbon it can be used both to adsorb pollutants from liquid or gaseous streams and to convert them to recyclable products. A highly-developed micropore structure is not required for all uses of activated carbon or a catalyst produced from it. A comparatively inexpensive ($325/ton projected) low surface area (<300 m^2/g) carbon has been developed at the Illinois State Geological Survey (ISGS) for cleaning incinerator flue gas. This grade of activated carbon is widely used in Europe for flue gas cleaning and for other applications. Activated carbon adsorbers of some type are required by recently passed U.S. Environmental Protection Agency (EPA) regulations for municipal waste combustors to control emission of cadmium, mercury, lead, dioxins, furans and acid gases (U.S. EPA, 1995). Similar regulations are expected for hospital and hazardous waste incinerators. The marketing of less costly activated carbons of the type used widely in Europe is expected in the United States. Low cost $OAC_{500\text{-}700}$ made from less expensive grades of activated carbon may become available for large scale adsorbent/catalyst systems designed to both remove and decompose toxic pollutants found in liquid and gaseous streams, chlorinated organic compounds in particular.

INTRODUCTION

$OAC_{500\text{-}700}$ has the potential to solve a number of environmental problems associated with misplaced organic chlorides. Chlorinated compounds in drinking waters and aquatic environments have become a significant topic for study by scientists concerned about effects of direct toxicity and/or carcinogenicity on human and aquatic life (Hanson, 1994). A correlation between surface water chlorination and cancer mortality rates in humans has been shown to be statistically significant (Kalmaz and Kalmaz, 1981). The chlorination of surface waters has been shown to produce high levels of trihalomethanes (THMs) (Bellar et al., 1974). Roughly 98% of this nations drinking water systems use chlorination. More than 300 chlorinated organic compounds have been identified in chlorinated potable waters, cooling waters, and sanitary effluents (U.S. Environmental Protection Agency (EPA), 1975). Activated carbons are needed to capture, concentrate, and decompose pesticides and THMs that are formed when the water is chlorinated (Graham and Ramaratnam, 1993). Regeneration with steam or superheated steam in the field is practical with low molecular weight volatile organic compounds (VOCs), but less volatile organics may require high temperatures (750-850°C) if regeneration of the expensive types of activated char now available is required.

The destruction of halogenated organics in wastes is another potential use of $OAC_{500\text{-}700}$. Halogenated organic compounds account for a major portion of toxic and persistent hazardous wastes. In Illinois, the General Assembly in 1981 passed a bill which prohibits landfill disposal of hazardous wastes effective January 1, 1987, unless the generator and disposal site operator can demonstrate that no reasonable alternative is available. In 1983, this schedule was accelerated for liquid hazardous wastes; P.A. 83-1078 prohibits landfill disposal of liquid hazardous wastes unless there is no reasonable alternative. A November 7, 1986, rule on solvents and dioxins began the phasing out of all landfill disposal of halogenated solvents. Methods which will convert some of this hazardous waste into recyclable chemical compounds are high priorities for the Illinois Hazardous Waste Research and Information Center (Miller, 1990).

The destruction of halogenated waste compounds is also a goal of the US EPA. A US EPA report describes an experimental project at Radian Corporation, Research Triangle Park, North Carolina, to validate the effectiveness of a treatment of halogenated waste compounds with a reagent composed of potassium hydroxide in a relatively small quantity of polyethylene glycol (Harden & Ramsey, 1986). It was effective in destroying the organic compounds chosen as being representative of low molecular weight compounds encountered in hazardous wastes including CCl_4, $CHCl_3$, CH_2Cl_2, $C_2H_4Br_2$, and CCl_3NO_2.

Potential uses of $OAC_{500\text{-}700}$ go beyond the problem of chlorinated organics. $OAC_{500\text{-}700}$ has recently been shown to catalyze other elimination reactions including the dehydration of alcohols, the deamination of amines and the dehydrosulfurization of mercaptans (Kruse et al., 1991).

BACKGROUND

Oxygen complexes control many of the properties of activated carbons (Boehm and Bewer, 1976; Leon y Leon D. and Radovic, 1994). An oxidized carbon catalyst of a type first described in the patent literature (Kruse and Ray, 1966) is the focus of this paper. It was initially produced by air oxidation of carbon blacks and activated carbons in the 500-700°C temperature range and is now designated $OAC_{500\text{-}700}$. It was effective for the dehydrochlorination of alkyl halides and promoted polymerization of chloromethyl aromatics (Kruse, 1969a). Incorporating potassium salts into the catalyst inhibited skeletal rearrangements of olefins produced from monochloro n-alkanes (Mahan et al., 1967). Continuous vapor phase dehydrochlorination of mixed linear C_{13}-C_{14} monochlorides gave >95% conversion for 690 hours (73.5 g of alkyl chlorides/gram catalyst) with $OAC_{500\text{-}700}$ produced from Darco activated charcoal (Kruse, 1969b). Engineers advising the inventors of this catalyst believed the costs would be too high for one-time use in a commercial plant. Regeneration was achieved with a steam-nitrogen mixture at 750°C but predicting the time needed to attain the desired precise amount of burn-off was difficult. Too much gasification shortened catalyst life. The regeneration method and the projected catalyst cost were among the factors that frustrated commercial development in the late 1960s. The commercial price of activated carbons marketed in the United States remains high today, at approximately $0.40 to dollars/pound (one to a few dollars/kg) and $OAC_{500\text{-}700}$ manufactured from them will bear the same high cost liability of the 1960s.

Not all processes require the expensive, high surface area adsorbents that dominate the U.S. domestic market. STEAG's a/c/t™ process is one of the processes being offered for licensing in the United States to clean incinerator flue gas. It does not require a sorbent with a N_2 BET surface area greater than 300 m^2/g (Bruggendick, 1993). The spent sorbent from STEAG's process is not regenerated, and regeneration may not be necessary with other processes using lower cost, lower surface area activated carbon. The state of Illinois through its Illinois Clean Coal Institute has demonstrated that an activated carbon satisfactory for use in STEAG's process can be produced from Illinois coal (Kruse et al., 1995b). The projected price by the ISGS for this sorbent, if produced in a dedicated plant having an 80,000 tons/year capacity, is $325/ton ($0.35/kg).

The price of the adsorbent (herdofenkoks) used by STEAG's European licensees is about $0.15/lb ($0.33/kg). This less costly activated carbon adsorbent has been available in Europe for several decades. Adsorbents of this type, made from brown coal, are known in Germany as F-coal and in Russia as S-coal (Smisek, 1970). They are used in technical applications for which cost and not adsorption capacity is the primary concern. This is the case when the active life of the material is for some reason low and replacement is not dictated by inadequate adsorption capacity. For example, the desulfurization of industrial gases using activated carbon is effective because activated carbon catalyzes the reaction

$$2\,H_2S + O_2 \text{ --> } 2\,H_2O + 2\,S + 106 \text{ kcal}$$

The sulfur, deposited in the pores of the active carbon, is extracted when the hydrogen sulfide in the gas exceeds a prescribed limit. Gas-adsorption active carbons are not suitable for this purpose. For this use, the important factor is not a highly developed microporous structure, but the number of macropores. The best results are obtained with F-coal.

DISCUSSION

A two step method for producing $OAC_{500\text{-}700}$ is a recent development (Kruse, 1995). The discovery that the oxidation of an activated carbon with boiling nitric acid followed by desorption of most of the CO_2-forming oxygen complexes in an inert atmosphere produces $OAC_{500\text{-}700}$ was a by-product of other research. During a study to determine the effect of oxygen complexes on the selective adsorption of targeted compounds from water, a series of carbons having differing levels of oxygen complexes was prepared by thermally desorbing CO_2 and CO from oxygen complexes introduced by nitric acid oxidation (Feizoulof et al., 1993). Adsorption isotherms for p-nitrophenol (PNP) were determined for the series of carbons and plots were made of the data using the Freundlich equation. The slope of the line generated in these plots is a measure of the strength of adsorption. The strength of the adsorption of PNP went through an unexpected maximum between desorption temperatures of 425°C and 725°C; material desorbed at 525°C had the highest slope (figure 1a). The adsorption tests were then repeated with carbons produced by desorption at 475°C, 525°C, 575°C and 625°C. The strongest adsorption was at 575°C (figure 1b).

Initial catalyst work by the author in the 1960s showed that the oxygen complexes put on below about 300-400°C did not produce dehydrohalogenation catalysts. Heating to 800°C destroyed the catalyst properties. A temperature of 600°C was an ideal mid range temperature for producing the active catalyst. Because temperature programmed desorption (TPD) in the recent studies showed the oxygen complexes on materials produced by the two methods, i.e., air (or dilute oxygen) oxidation (figure 2 e,f) and the two step oxidation/desorption method (figure 2 b,c) were similar and the strength of the adsorption of PNP went though a maximum at the preferred temperature (600°C) for producing the catalyst with air, comparisons of catalyst

activity were made. The percent conversion in a vapor phase dehydrochlorination of 1,1,2,2-tetrachloroethane at 450°C over a bed of the test material was the measure of catalyst activity (Fatemi et al, 1993). The material produced by desorption of oxygen complexes at 500-700°C was indeed a good catalyst (Kruse et al., 1995a). It appears that CO-producing oxygen complexes are essential and that the CO_2-producing complexes that are desorbed by heating to 500°C reduce catalyst activity. A similar effect for catalyzing oxidation reactions was stated by Boehm et al. (1984), "enhancement could sometimes also be observed after chemisorpiton of oxygen. There was no clear-cut picture in this case, however, the general impression is that catalytic activity is enhanced by basic surface oxides, whilst acidic surface oxides are inhibitory".

The adsorption properties of the starting activated carbon are modified but not lost by making it a catalyst. Most of the initial carbon's adsorption capacity is available to remove a variety of pollutants from liquid and gas streams and, in addition, $OAC_{500\text{-}700}$ has the potential to convert many classes of pollutants to recyclable compounds (Kruse et al., 1992; Beaulieu et al., 1992; Fatemi et al., 1993; Feizoulof et al., 1993).

COMMERCIALIZATION

Important factors for future commercial development of $OAC_{500\text{-}700}$ include (1) how it ranks in competing tests with other catalysts, (2) comparative disposal costs and (3) availability and pricing. Porous glass (unglazed porcelain) (Lycourghiotis, 1976), silica gel, (Misono, 1973, Lycourghiotis et al., 1981; Mochida et al., 1981; Suarez and Mazzieri, 1987), B-18 crown ether-potassium chloride on silica gel (Fujitsu et al., 1985), alcoholic potassium hydroxide, and the new Calgon carbon catalyst, Centaur, are among its rivals. Extensive comparative tests of $OAC_{500\text{-}700}$ and other catalysts will be necessary to determine the strengths and weaknesses for specific applications. The disposal costs must be weighed against regeneration costs. Incineration appears an option for $OAC_{500\text{-}700}$ and Centaur not available to other catalysts. It remains to be seen how much the price of Centaur (about $2.50/pound today) will decrease with large scale production.

The estimated production capacity of activated carbon in the United States, which currently has N_2 BET surface areas from 500-2500 m^2/g, was estimated in 1990 to be 146,000 metric tons (Baker et al., 1992). Retrofitting only a fraction of the existing incinerators with carbon-based systems would create a demand greater than exists today for all types of activated carbon. Because of the number of grades of activated carbon marketed today, the prices reflect fine chemicals prices, often in dollars per pound. With the arrival of dedicated facilities for producing 80,000 ton/year or more of one type of activated carbon, the prices can be expected to decline, whatever the grade of activated carbon marketed. The future cost of $OAC_{500\text{-}700}$ should parallel the decreasing prices of activated carbon marketed in the Unied States.

CONCLUSIONS

The high cost of many technically feasible systems for protecting the environment prevents serious consideration of their use. Providing the data base on lower cost adsorbents and catalysts will promote their commercial availability in the future. A low temperature oxidation/desorption sequence has been developed; this process is not only more readily managed than air oxidation at 500-700°C for producing $OAC_{500\text{-}700}$ dehydrochlorination catalyst but may also be adaptable to regenerating the catalyst activity of fixed beds in place. The projected availability of lower cost activated carbons means lower cost $OAC_{500\text{-}700}$ produced from them. There are many areas where organic halide capture and destruction can be tested for addressing environmental pollution problems. The recycling of hydrocarbons that are produced by removing hydrogen chloride, water and hydrogen sulfide from a host of organic compounds would support the growing emphasis on recycling misplaced and spent materials.

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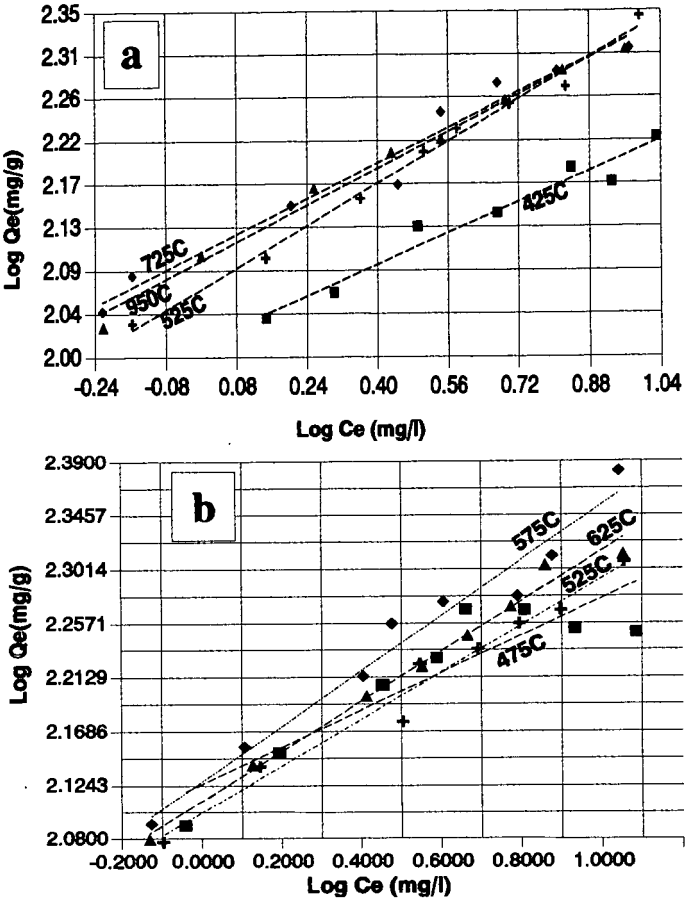

Figure 1. Freundlich equation plots for p-nitrophenol on HNO_3-oxidized activated carbon desorbed to the temperature shown.

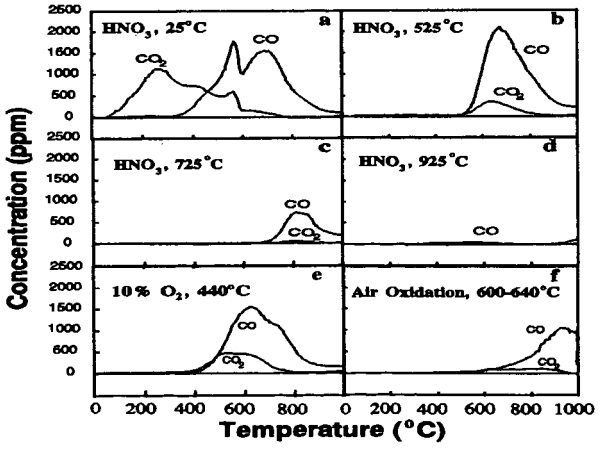

Figure 2. TPD profiles of HNO_3-oxidized chars desorbed at 25°C to 925°C and oxygen oxidized samples.

IMPROVED GRANULAR ACTIVATED CARBON FOR THE STABILIZATION OF WASTEWATER PH

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Keywords - pH stabilization, Granular activated carbon, Carbon oxidation

ABSTRACT

Laboratory studies have identified the cause of the pH rise, which occurs during water treatment with activated carbon, as an interaction between the naturally occurring anions and protons in the water and the carbon surface. The interaction can be described as an ion exchange type of phenomenon, in which the carbon surface sorbs the anions and corresponding hydronium ions from the water. These studies have shown that the anion sorption and resulting pH increase is independent of the raw material used for the activated carbon production, e.g. bituminous or sub-bituminous coal, peat, wood or coconut. Also, the pH excursions occur with virgin, reactivated, and acid washed granular carbons. Current pH control technologies focus on adjustment of the wastewater pH prior to discharge or recycle of the initial effluent water until the pH increase abates. However, improved water pH control options have been realized by altering the carbon surface through controlled oxidation rather than the water chemistry or extended preprocessing at the treatment site.

INTRODUCTION

Many times, the start up of granular activated carbon adsorption systems for the control of organic contaminants in wastewater exhibits unacceptable increases in the adsorber effluent pH. This increase can result in an effluent pH exceeding NPDES permits. Experience shows that the duration of the pH increase ranges from several hours to several days, during which time several hundred bed volumes of water can be discharged with a pH in excess of 8.5 to 9, which are typical high limits on discharge pH.

Historically, the methods used in the remediation of the high pH effluent were to treat the effluent with acid to lower the pH, to backwash the system for extended periods of time, or to recirculate the water until the pH rise naturally abated. Obviously, an incentive exists to remediate the problem with methods other than the extensive and expensive ones mentioned here. As a result, a program was begun to identify the cause of the pH excursions and provide a cost effective remediation to the problem.

EXPERIMENTAL

The activated carbons used in this experimentation were both virgin and reactivated, acid washed and non acid washed, and produced from a wide variety of raw materials. The water used in the experimentation was either tap water from the Robinson Township Municipal Authority, a suburb of Pittsburgh, or ultra pure Milli-Q Plus water (Millipore Corp. Bedford, MA). Additionally, when examining specific anion effects, the sodium salt of sulfate, chloride, or nitrate was added to the Milli-Q water. These salts were Fisher ACS grade or equivalent.

pH measurements were performed following Standard Methods[8]. Anion analyses were performed with a Dionex Model 14 Ion Chromatograph (Dionex Corp. Sunnyvale, CA). Cation analyses were performed using atomic absorption spectroscopy.

The experimental apparatus consisted of a one inch ID x 12 inch L Pyrex glass column through which the water was pumped upflow with a Masterflex peristaltic pump and tygon tubing. Each carbon was boiled in Milli-Q water for 15 minutes, cooled to room temperature, and then transferred to the column. The water flow rate provided approximately 7.5 minutes empty bed contact time (EBCT), and discrete samples were collected for analysis. For the anion specific experiments, the water was prepared in a seven gallon, glass carboy.

The oxidized carbons were prepared at both high and low temperature with air as the oxidant.[4,5,6] Carbon pH measurements on both oxidized and non-oxidized carbons were performed by gently stirring 25 g of carbon in 100 mL of a sodium sulfate solution (80 mg sulfate/L) for 30 minutes. This procedure is referred to as the modified contact pH.

RESULTS AND DISCUSSION

Effect of Water Quality

The extent and duration of the pH excursion depends upon the water quality. Using Filtrasorb 200 as the test carbon in this simulation, the water was varied from tap to Milli-Q water. Figure I shows that tap water from Robinson Township, PA yields a pH rise up to 10. With the Milli-Q water, the excursion is very limited, i.e. 40 bed volumes when the pH drops below 8.5. However, the pH excursion can occur with Milli-Q water through the introduction of any of a number of anions. Shown in Figure 1 is the effect of sulfate addition on the pH spike. Adding 80 mg/L of sulfate causes the pH spike to return and the pH profile closely matches that of tap water. (Throughout this discussion, 8.5 pH is chosen as the reference point for a pH excursion.)

The type of anion does not have a significant effect on the excursion, and concentration only affects the pH profile at low anion concentrations. Table 1 highlights the excursion that occurs as the anion concentration and anion changes. When the anion changes from sulfate to chloride to nitrate, the impact of the anion is negligible with the pH peak occurring around 10 and the excursion lasting about 400 BV. Only at very low concentrations does the pH spike become muted. The loading of the anions ranges from 3.3 to 4.3 mg/L after treating 400 bed volumes of water. Cations were not removed by the carbon.

Effect of Carbon Type

A pH excursion has been shown to be independent of the raw material and whether or not the carbon is acid washed. Figure 2 shows that whether the carbon is prepared from bituminous or sub-bituminous coal, coconut, wood, or peat each carbon exhibits an increase in pH when the carbon is brought on line. This same conclusion results when the carbon is acid washed and also following reactivation.

Hypothesized Mechanism

It is believed that the pH excursions are a function of the activated carbon surface that results from the high temperature activation or reactivation process. Huang[1] broadly classifies activated carbons as H or L types of carbon. In these broad categories, an H-type carbon, produced at high temperature in a reducing atmosphere, adsorbs strong acids while L-type carbons, produced by surface oxidation, adsorb strong bases. Thus, adsorption of "acid groups" as witnessed by Snoeyink[2] may be responsible for upsetting the water equilibrium. This adsorption may actually be protonation of pyrone type surface oxides (Leon y Leon[3]) or other structures on the carbon surface. Following protonation, the surface is charge neutralized with the sulfate, chloride, or other anions which may be present in the water. In absence of these ions, the neutralization of the surface occurs with the hydroxide ions that result from hydrolysis of water which initially yielded the protons. It may actually be more accurate to say that the anions (sulfate, chloride, etc.) exchange with the hydroxide ions following protonation; however, additional testing will be required to conclusively determine the mechanism.

pH Stabilization with Oxidized Carbons

An effective remediation of the pH increases is accomplished through the controlled oxidation of the activated carbon surface, prior to treating the water, which alters the carbon surface to stabilize the effluent water pH. Two methods have been developed to achieve this. First, an elevated temperature oxidation[4,5] provides surface oxides that inhibit the ion exchange phenomenon and stabilize the pH. Likewise, a low temperature oxidation also effectively stabilizes the water pH[6].

When carbon prepared by either of these methods is exposed to water, the excessive pH rise in the effluent water is eliminated. Figure 3 shows that both the high temperature and low temperature oxidized pH stable carbons can keep the effluent water pH at or below the target pH of 8.5. Further, effluent water pH stabilization can be accomplished for both the synthetic water prepared with Milli-Q water plus sulfate and also tap water, which had an initial pH of 7.8. The two stabilized pH profiles were developed with virgin carbon (Milli-Q plus 80 mg/L sulfate) and reactivated carbon (tap water) which demonstrates that the oxidation processes are applicable to both virgin and reactivated carbons. The modified contact pH of the oxidized virgin carbon was 7.4 while the oxidized reactivated carbon had a modified contact pH of 8.5. Finally, Carr and Farmer[7] demonstrated that pH stabilized carbons can be implemented easily in full scale systems.

Surrogate pH Stable Carbon Test

A modification has been made to a standardized pH test to predict whether a carbon will exhibit a significant pH rise. The standard test contacts carbon with deionized water. With this test, most carbons will have a contact pH between 6 and 8. However, by adding sulfate to the deionized water, greater pH changes can occur, and the test can be used to predict whether the carbon will

cause a rise in the effluent water pH. Table 2 shows that carbons with a modified contact pH above about 9 will exhibit a pH increase. Also, with the exception of the wood base carbon, as the modified contact pH decreases, the duration of the pH increase generally decreases.

SUMMARY AND CONCLUSIONS

Stabilization of the effluent water pH has been demonstrated through the use of oxidized granular activated carbons. This oxidation can be accomplished at both low and elevated temperatures through the use of air, oxygen, or other suitable oxidants and is applicable to both virgin and reactivated carbons. Prediction of the ability of a carbon to stabilize the effluent water pH is also possible through the use of the modified contact pH test.

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Table 1. Effect of Anion and Anion Concentration on Effluent pH Profile

Anion	Concentration mg/L	Maximum pH	pH Excursion Duration Bed Volumes	Anion Loading mg/g GAC
Sulfate	80	10.5	360	4.3
Chloride	18	10.2	420	3.3
Nitrate	5.3	9.8	>410	3.9
Sulfate	1	9.4	220	0.73

Duration of the pH spike represents volume of water treated until pH $\leq$ 8.5
Water used was Milli-Q water spiked with the referenced amount of anion
Anion loading is represented as mg anion/g GAC after treating 400 bed volumes

Table 2. Modified Contact pH and Extent of pH Excursion

Activated Carbon	Modified Contact pH	pH Excursion Duration (Bed Volumes)
Bituminous	10.4	350-400
Sub-bituminous	10.4	350
Peat	11.1	460
Coconut	10.3	200-250
Bituminous-acid washed	9.8	200-250
Wood	9.6	550
Reactivated bituminous	10.6	400
pH Stable	8.2	0

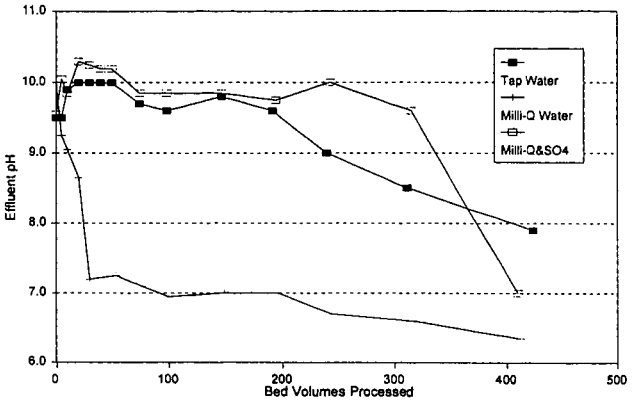

Figure 1. Effect of Water Quality on pH Profile - Bituminous Carbon

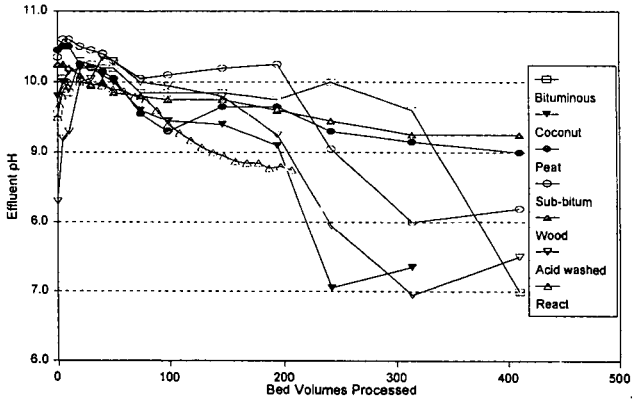

Figure 2. Effect of Carbon Raw Material on pH Profile - Milli Q Water & Sulfate (80 mg/L)

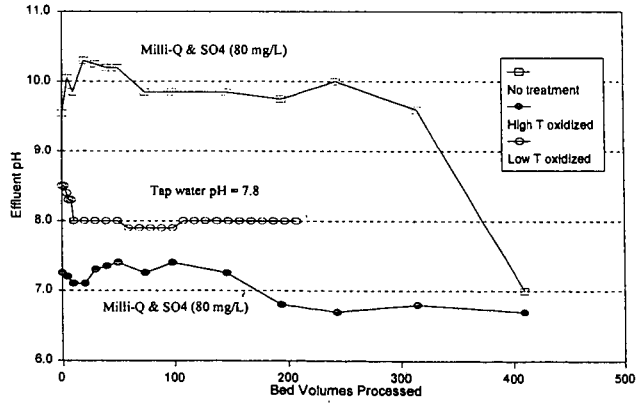

Figure 3. Effect of Oxidized Carbon on pH Profile - Bituminous Carbon

EFFECTS OF SURFACE CHEMISTRY OF ACTIVATED CARBON ON THE ADSORPTION OF AROMATICS CONTAINING ELECTRON-WITHDRAWING AND ELECTRON-DONATING FUNCTIONAL GROUPS

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KEYWORDS: activated carbon, adsorption, organics, surface chemistry.

INTRODUCTION

Adsorption of organic water pollutants onto activated carbon surfaces has been studied extensively and a voluminous literature is available on this increasingly important practical problem [1,2]. There are many well established facts; there are also some conflicting data. More importantly, conflicting interpretations have been offered and no attempt seems to have been made to reconcile them. Because many of the pollutants are weak electrolytes, the central fundamental issue is how to account for the well documented importance of (a) the pH of the aqueous solution, and (b) the surface chemistry of the adsorbent.

In an early study, Getzen and Ward [3,4] presented a Langmuirian theoretical framework for the adsorption of both ionic and molecular adsorbate species as a function of pH. Their approach provided an explanation for the often observed maximum in adsorbate uptake at pH = pK_a, without explicitly taking into account the changes in the surface chemistry with pH. The explanation for an acid adsorbate is as follows: as pH decreases toward the pK_a value, H^+ ions as well as organic anions are adsorbed on the surface. Since the concentration of H^+ rapidly exceeds that of the weak electrolyte anions, the former adsorb on the carbon surface far in excess of the anions and subsequently enhance anion adsorption. However, because the concentration of anions decreases as pH increases, a point of diminishing returns is eventually reached and a maximum in adsorption uptake is observed.

In another milestone study, Müller *et al.* [5-7] used the same approach based on Langmuirian competitive adsorption of ionic and molecular species, but accounted explicitly for the pH-induced variations in the adsorbent surface charge. This allowed them to provide a more rigorous explanation of the adsorption maximum at pH = pK_a in terms of both adsorbate and adsorbent properties. It is necessary that considerable ionization of the adsorbate (solute) take place while the surface still possesses a charge that is opposite to that of the ionic solute. In particular, for an acidic solute, it is necessary that, for a given pH increment, the magnitude of the slope of the solute dissociation curve be larger than that of the surface potential curve.

Our interest in this topic [8,9,10] stems from the realization [11,12] that the lack of understanding of adsorption of inorganic solutes on carbons has suffered for many years from a lack of appreciation of the amphoteric nature [13] of carbon surfaces. Based on intriguing results for adsorption of benzoate, oxalate and fumarate anions on chemically modified (oxidized vs. nitrided) activated carbons [14], we proposed the following mechanisms of adsorption: (a) adsorption of benzoate (aromatic) anions occurs primarily on the basal plane of carbon and the electron-withdrawing effects of nitrogen and carboxyl functional groups suppress the interaction of the basal planes with the adsorbate's aromatic rings; (b) adsorption of aliphatic anions occurs also predominantly on the basal plane and the same electron-withdrawing effects enhance its interaction with the carboxyl anions. More recently, we have begun to study in some detail the relative importance of dispersion and electrostatic adsorbate/adsorbent interactions as we examined the uptake of methylene blue and p-nitrophenol, as well as benzoic acid and oxalic and fumaric acids [15]. We concluded that, while electrostatic interactions are important, π-π dispersion interactions appear to be dominant in the adsorption of aromatic solutes. On the other hand, electrostatic repulsion appears to be much more important for the adsorption of aliphatic anions. These are important and arguably novel findings, and their further investigation (and substantiation) is of interest.

In the present study, we contrast the behavior of chemically different carbons in adsorbing two vastly different aromatic solutes: nitrobenzene is a very weak Lewis acid that possesses the electron-withdrawing NO_2 group, while aniline is a predominantly cationic species at pH < 4.6 which also possesses the electron-donating NH_2 group.

EXPERIMENTAL SECTION

Two commercial granular carbons, NORIT GCW and Calgon BPL, were used as the adsorbents. Oxidation of GCW was performed by contacting the sample with concentrated HNO_3 at 363 K for 6 h. The sample was washed until neutral pH was achieved, and dried at 380 K before use. The reaction with NH_3 (nitriding) was carried out in a tubular furnace flushed at a flow rate of 30 cc/min. The temperature was kept constant for 3 h. Prior to use, the sample was washed and dried. Devolatilization of the carbon was achieved by heat treatment in inert atmosphere at 1173 K. Elemental analysis of the samples was performed using LECO CHN-600. Maximum nitrogen incorporation was observed at 673 K.

The isoelectric point (IEP) and the point of zero charge (PZC) were measured by electrophoresis and mass titration, respectively. The IEP was determined with a Zeta-Meter System 3.0+ apparatus, using 10^{-3} M KNO_3 as the indifferent electrolyte; the plateau in the plot of equilibrium pH of the slurry vs. solid weight fraction identified the PZC of a carbon. Additional chemical surface characterization of the as-received and modified carbons was attempted briefly using XPS (ESCALAB 200A-VG). Physical surface properties of the carbons were determined using an Autosorb adsorption apparatus (Quantachrome).

Adsorption isotherms were obtained by adding different amounts of carbon to Nalgene flasks containing 0.1 g/L of aniline or nitrobenzene. The pH was adjusted with NaOH or HCl. The suspensions were shaken until equilibrium was reached (ca. 24 h), and the residual adsorbate concentrations were measured by uv spectroscopy.

RESULTS AND DISCUSSION

Table 1 summarizes the physical and chemical characteristics of the GCW samples used. For both nitrided and oxidized samples no drastic changes in surface area or micropore volume were observed, in agreement with our previous studies [12,14]. Curiously, for a nitrided sample that had been oxidized previously, a higher N incorporation (~7 wt%) was achieved (at 658 K for 3 h) at the expense of a drastic decrease in BET surface area (~300 m^2/g).

The values of PZC were consistently higher than those of IEP, in agreement with previous studies [12,14]. They indicate surface charge inhomogeneities within the carbon particles [12,14]. More recently, this difference between IEP and PZC values, i.e., the combination of electrophoresis and mass titration, was shown to be a powerful tool for the analysis and design of surface chemistry of active carbons, especially for determining the spatial (radial) distribution of the acidic oxygen functional groups within carbon particles [16].

Deconvolution of the broad and complex N1s XPS peaks of nitrided carbon [10] suggests the presence of pyridine (or nitrile groups), as well as amide, amine and pyrrole groups.

Figures 1-3 show the behavior of the different carbons in adsorbing aniline under widely varying solution chemistry conditions. A significant effect of solution chemistry (pH) on the uptake is observed for both as-received and modified carbons. The effect of carbon surface chemistry is seen to depend on pH. The uptakes at pH≤PZC are enhanced by surface oxidation; at pH=11 the effect is much less pronounced.

Figures 4-6 show the behavior of the different carbons in adsorbing nitrobenzene. In contrast to the findings for aniline, solution chemistry (pH) had little effect on the equilibrium uptakes. The effect of surface chemistry is seen to be much more important. The as-received and devolatilized carbons had the highest uptakes, while adsorption was suppressed for both nitrided and oxidized carbons.

Some of the phenomena observed in the present work were observed in the published literature. Some of them were also misinterpreted, as argued in more detail elsewhere [2,10]. The principal reason for these misinterpretations is the failure to recognize the amphoteric nature of carbon surfaces and its effects on electrostatic adsorbate/adsorbent interactions. For example, in a large number of studies it is assumed that the carbon surface acquires a net negative charge over a very wide range of pH conditions [17]. A typical example of the resulting inconsistencies is a discussion of phenol adsorption by Grant and King [18]. They observed a significant increase in reversible phenol uptake as the pH was reduced from 12.1 to 8.0, and then to 1.8. This was tentatively attributed to changes in phenol activity with decreasing pH. A more straightforward explanation (apparently discarded by the authors) - which is thought to explain the vast majority of phenol adsorption data [2] - is the one based on the work of Müller et al. [5-7]. At the high pH of 12.1 (pH>pK_a, pH>PZC), the low uptake is due to the electrostatic repulsion between the negatively charged carbon surface and phenolate anions. At pH=8.0

(pH<pK_a), 99% of the adsorbate exists as phenol molecules, and 1% as phenolate anions; at the same time, the degree of dissociation of acidic groups decreases and there is a better balance between positively and negatively charged sites on the surface. At low pH (e.g., pH<3), most carbons are positively charged, at least in part as a consequence of donor/acceptor interactions between the graphene layers and the hydronium ions [19]. In agreement with these arguments, for BPL carbon we observed similar uptakes of aniline at pH>PZC (pH=6.0-10.8) and a drastic decrease at pH=1.5.

The importance of dispersive interactions is also apparent in Figures 1-6. For example, aniline is much more soluble in water than nitrobenzene (35 vs. 2 g/L at 25 °C); yet its uptake does not reflect this. This is attributed to the beneficial effect of the electron-donating NH_2 group. Enhanced adsorption of aniline is due to the resulting increase in the negative charge density on the graphene layers of the adsorbent. Similarly, both oxidation and nitriding of the carbon (which have opposite electrostatic effects) reduce the π electron density on the graphene layers and have a negative effect on the uptake of nitrobenzene, in agreement with our results with benzoic acid [14]. Furthermore, neutralization of oxygen functional groups produced no significant effect on the uptake of nitrobenzene [10].

ACKNOWLEDGMENTS

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Table 1
Characteristics of GCW Carbons Used

Sample	C (wt%)	H (wt%)	N (wt%)	O (wt%)	S_{N2}* (m^2/g)	V_{mi}** (cc/g)	IEP	PZC
As received	96.5	0.57	1.29	1.64	859	0.62	4.0	8.0
Devolatilized	98.0	0.41	1.46	0.13	858	0.58	5.5	10
Oxidized	82.9	1.30	1.60	14.2	807	0.55	1.5	2.6
Nitrided	90.5	0.47	5.81	3.22	869	0.59	5.2	8.9

*BET surface area;

**micropore volume obtained from the Dubinin-Radushkevich equation applied to the N_2 adsorption isotherm.

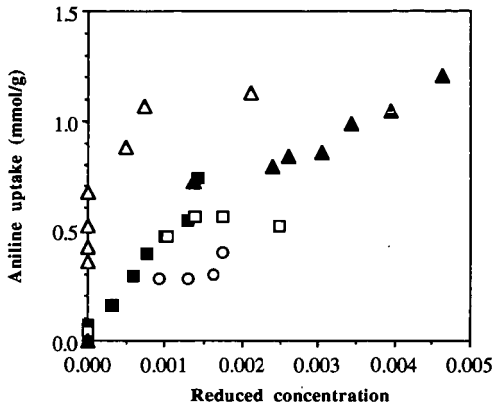

Figure 1. Aniline adsorption isotherms at pH=2 for different carbons:
■ , as-received(1); □ , as-received(2); ▲ , devolatilized; ○ , nitrided; Δ , oxidized.

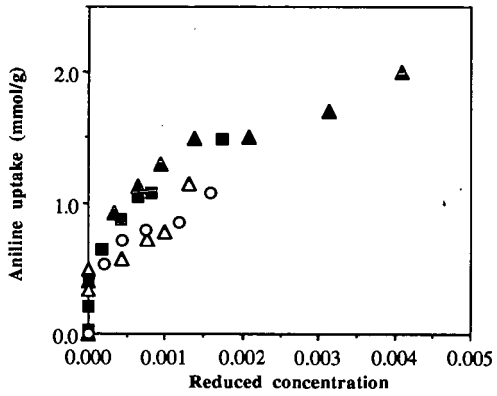

Figure 2. Aniline adsorption isotherms at pH=11 for different carbons:
■ , as-received; ▲ , devolatilized; ○ , nitrided; Δ , oxidized.

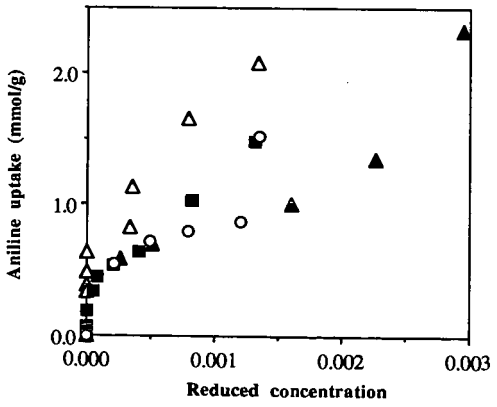

Figure 3. Aniline adsorption isotherms at pH=PZC for different carbons:
■ as-received; ▲ , devolatilized; ○ , nitrided; Δ , oxidized.

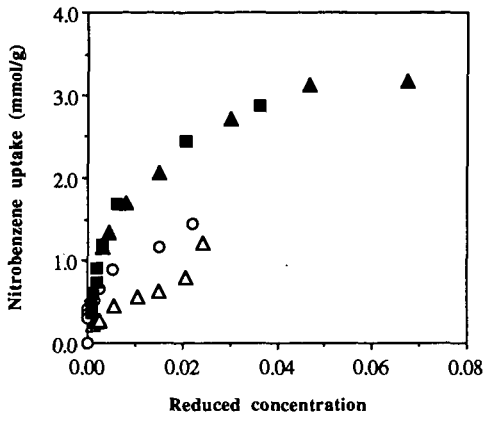

Figure 4. Nitrobenzene adsorption isotherms at pH=2 for different carbons: ■, as-received; ▲, devolatilized; ○, nitrided; Δ, oxidized.

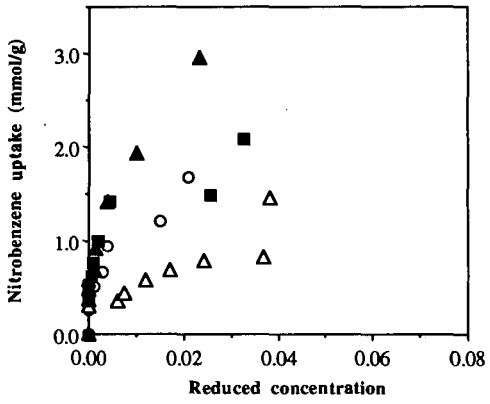

Figure 5. Nitrobenzene adsorption isotherms at pH=11 for different carbons: ■, as-received; ▲, devolatilized; ○, nitrided; Δ, oxidized.

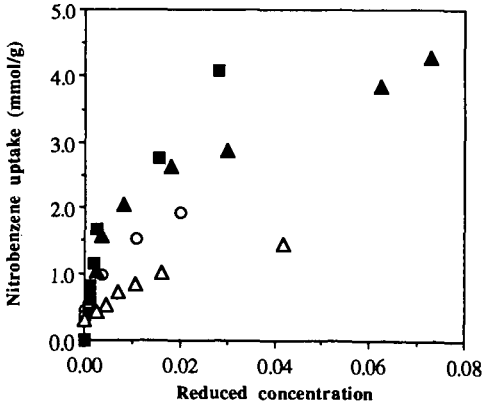

Figure 6. Nitrobenzene adsorption isotherms at pH=PZC for different carbons: ■, as-received; ▲, devolatilized; ○, nitrided; Δ, oxidized.

GRANULAR ACTIVATED CARBON AS A TOXICITY REDUCTION TECHNOLOGY FOR WASTEWATER TREATMENT

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Keywords: toxicity reduction, activated carbon, use rate

Introduction

The Clean Water Act governs the discharge of wastewater to all navigable waterways in the U.S. It is the explicit purpose of this Act to prevent the discharge of "toxic pollutants in toxic amounts" to the nation's surface water supplies. To achieve this goal, the National Pollutant Discharge Elimination System (NPDES) was established, whereby a facility wishing to release wastewater to a surface water system must obtain a permit to do so. This NPDES permit contains the wastewater quality criteria that must be met before the wastewater can be legally discharged.

Historically, specific chemical limits have been used for establishing the quality of a wastewater discharged from a facility. The EPA developed a list of priority pollutants for which maximum discharge concentration limits were established. This regulatory approach had the advantage that straightforward protocols with clearly defined quantification limits were available for compliance and testing purposes. However, it became increasingly apparent that there were weaknesses with this approach when it was used exclusively. Many chemicals not included in the priority pollutant list will produce toxic responses from indigenous biota when released to a surface water. Therefore, the EPA developed methods for directly assessing the potential toxicity a discharge may generate in a receiving stream. The protocols and techniques for performing toxicity tests have been refined to the point the EPA is comfortable including them as another method for regulating the quality of a permitted discharge [1,2,3].

As a result, there is now increased attention on quantifying the toxicity, or potential toxicity, of wastewaters from industrial facilities and publicly owned treatment works (POTWs). Therefore, as these facilities renew their NPDES permits, toxicity testing and/or toxicity limits are being increasingly introduced. Since biological systems are often more sensitive to pollutants than can usually be quantified by conventional analytical methods, dischargers are faced with achieving more stringent water quality goals.

This paper will present several case studies to illustrate how certain facilities have used granular activated carbon (GAC) to achieve compliance with these more stringent regulations.

What Is Toxicity?

Toxicity is operationally defined as any adverse biological effect [4]. It is classified as either acute or chronic in nature. The adverse effect monitored for acute toxicity is organism death, while chronic toxicity can be any deviation from normal growth or behavior for an organism. Toxicity may be reported as a concentration (or the percent solution of wastewater mixed with a control water), as Toxicity Units, or as "% Survival." Tests for determining acute toxicity are usually shorter in duration than those for chronic toxicity. Acute tests are typically completed within 48 hrs, while chronic tests may last much longer (full chronic tests could last a year or more). Table 1 presents a comparison of acute and chronic testing. Dischargers that have acute tests in their current permits may have more sensitive species or chronic tests included when their permits are renewed. Chronic criteria are often more difficult to satisfy than acute criteria. Thus, the inclusion of a more sensitive specie or a chronic test means the discharger is again faced with a more stringent effluent quality requirement.

Resolving Toxicity Problems

A facility that expects to receive toxicity limits or toxicity test requirements may do preliminary testing to determine whether they will have a compliance problem. If the results indicate the presence of unacceptable levels of toxicity, a "Toxicity Reduction Evaluation" (TRE) must be completed to determine how to eliminate or reduce the toxicity to acceptable levels. A TRE can be very time consuming and costly, particularly if a complex wastewater is involved. Figure 1 presents a schematic of the steps involved in a TRE.

Included in the TRE is a systematic attempt to identify the chemical(s) causing the toxicity. This so-called "Toxicity Identification Evaluation" (TIE) can have one of three outcomes [5]; 1.) a specific chemical is identified, 2.) a particular wastewater fraction is consistently identified as toxic, or 3.) no specific chemical or fraction is consistently identified as causing the toxicity.

If (1) is the outcome, it is a straightforward matter to design treatment systems to remove specific contaminants. If (2) or (3) is the outcome, it becomes more difficult to choose an appropriate

treatment technique and considerable effort will be required to prove the best alternative(s). However, if organics are implicated as a source of toxicity, activated carbon should be considered as a toxicity reduction technology.

To illustrate this point, several case studies will be reviewed below. These studies include three oil refineries and a chemical manufacturing facility. In some cases, studies were not optimally designed, while others were. Also, one of the examples is of a successful program that subsequently required optimization.

CASE STUDY 1 - REFINERY A

Refinery A treats a sour crude oil. It became apparent that toxicity testing using Daphnia would be included when they renewed their NPDES permit. Their treatment system consisted of pH adjustment and a equalization/bio-treatment pond and would not produce an effluent complying with the new permit. A series of toxicity reduction treatability studies were begun, rather than a systematic TRE, to determine what methods might remove the toxicity. The technologies tested as tertiary treatments to Activated Sludge (AS) processes were ClO_2, H_2O_2, O_3, and GAC. Table 2 presents the results of the batch tests completed with these technologies. The results indicated that AS and or Activated Sludge-Powdered Activated Carbon (AS-PAC) followed by ClO_2 or H_2O_2 actually increased their toxicity. However, tertiary treatment with O_3 or GAC reduced the effluent toxicity to satisfactory levels. Unfortunately, because a treatability-based toxicity reduction approach was used rather than an organized TRE which included a TIE, the presence of NH_3 excursions in the refinery caused inconsistent results in some aspects of the study. Thus, it was decided that an AS system with PAC addition could provide sufficient performance during the interim while sources of NH_3 were traced and reduced. The addition of GAC polish would be considered if operational experience showed that it was needed to ensure compliance. GAC was chosen over O_3 due to its cost effectiveness.

CASE STUDY 2 - REFINERY B

Refinery B processes heavy crudes. The wastewater treatment system consisted of API separators, DAF units, an aerated bio-pond and clarification pond. This refinery was informed that a sensitive toxicity test (a 96 hr flow through trout test) was going into their renewed permit. Due to the timing of the permit renewal, the refinery did not attempt to evaluate any toxicity reduction technologies. Instead, a survey of similar facilities with similar permits was made and GAC was found to be the preferred technology. Thus, while installation of a full scale GAC system proceeded, a pilot study was conducted to prove GAC worked and to determine the GAC use rate. Table 3 provides a description of the pilot system and Figure 2 presents the study results. A GAC use rate of 0.4 lb/1000 gal was determined in the pilot study for this refinery. Due to improved performance from their bio-treatment system over time, the full scale system has operated at an even lower use rate.

The refinery did not stop at this point. In anticipation of stricter limits in the future, a TIE is underway at the refinery to determine what the toxicants are and where they are generated. The plan now is to reduce the toxicity at the source an improve the GAC use rate further. An optimization of the GAC system may occur in the future, as a result.

CASE STUDY 3 - REFINERY C

Refinery C treats heavy crudes. The wastewater system included API separators, DAF units, coagulation and biological treatment. However, a polish operation was needed to achieve compliance with the refinery's acute toxicity limits for 3-spined stickleback. After some preliminary screening studies, GAC was chosen as the technology for achieving compliance and a custom system was successfully installed and operated for the life of the permit.

When the refinery renewed its permit, after five years of compliance, a more sensitive specie (trout) was required for toxicity testing. As a result, the refinery had to re-evaluate the current system for compliance with new criterium, >95% survival for a 96 hr flow through trout test. An optimization study was initiated to determine whether the system could be operated more economically while still satisfying the new permit. Table 4 provides the operating conditions for the tests and Figure 3 illustrates the results of this optimization study. Result for the full-scale system under normal operation are included in Figure 3. A change in the operation of the full scale system was recommended to satisfy the new permit and provide a more cost effective use rate. The carbon use rate could be reduced from >2.5 lb/1000 gal to 1.7 lbs/1000 gal.

CASE STUDY 4 - SPECIALTY CHEMICAL PLANT

A chemical plant had to meet toxicity limits for two species, Daphnia and fathead minnows. Its wastewater treatment system consisted of pH adjustment, activated sludge, and clarification. The expected toxicity limits were exceeded for both species. A thorough TRE was completed and several treatment technologies were evaluated for toxicity reduction, as a result. However, only GAC consistently reduced the toxicity to acceptable levels. An extensive pilot study was completed to determine optimal operating conditions and other design information for a GAC system. Table 5 presents a summary of the pilot test conditions that evaluated performance at 30 and 40 gpm. Figures 4 and 5 present results for tests completed at 30 gpm.

The use rate for the 30 gpm test averaged 3.02 lb/1000 gal and the use rate for the 40 gpm averaged 1.62 lb/1000 gal. The apparent discrepancy between these two use rates is reflected by two differences between the tests. First, the activated sludge plant did a much better job removing toxicants during the 40 gpm tests. Second, a sand filter for solids removal was included in the 40 gpm study, which reduced backwash frequency and removed some toxicity which was attributable to the solids in the wastewater.

It was of interest to note in these case studies that toxicity breakthrough could not be unequivocally correlated to any of the routine monitoring parameters used at the facilities. Also, toxicity breakthrough did not correlate with specific chemical breakthrough. Thus, one of the challenges in operating a GAC system for toxicity reduction is deciding upon a monitoring method to determine change out. With flow through toxicity tests, monitoring between GAC vessels in series can be done and change outs based on a certain percentage of toxicity breakthrough in a lead bed. In other cases, a global parameter such as TOC or COD may consistently achieve 100% breakthrough before toxicity breakthrough. In these cases, the global parameters may be useful monitoring tools. Some facilities have successfully based change outs strictly on a timed schedule.

Table 6 summarizes the use rate information for the studies reported here by providing an estimate of the cost for treating the specific wastes. Overall, these results were such that they provided attractive economics, compared to other technologies, for the facilities that have installed or will install GAC for toxicity reduction.

Summary

The case studies presented have served to illustrate that GAC provides an effective, yet flexible means for reducing the toxicity of wastewater where organics are a source for at least some of the toxicity. Compared to alternate technologies, GAC has been shown to be cost effective in achieving compliance goals. It also offers the opportunity for further optimization should GAC be installed to achieve one toxicity goal and another more stringent goal is introduced at a later date.

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TABLE 1
Comparison of Acute and Chronic Toxicity Tests

Acute Toxicity	Chronic Toxicity
Effect observed is organism death. Usually is a short term test (<96 hr).	Effect observed can be growth inhibition, reduced reproduction, behavioral changes, or other life cycle changes. Full chronic tests may last 30 days - 1 yr. EPA subchronic tests usually last 4-8 days.
Advantages Standardized protocols Relatively rapid and less expensive Endpoint easy to identify	Advantages More sensitive than acute tests Assess parameters other than death
Disadvantages Indicates only fatal concentrations Assumes fast acting toxicants May not reflect real world exposure	Disadvantages More costly and time intensive than acute End points more difficult to recognize More difficult protocols

TABLE 2
Results of Tertiary Treatment Technologies After AS for Refinery A

Treatment	Average % COD Removal	Effect on Toxicity Chronic	Acute
O_3	5.8	decreased	decreased
H_2O_2	-13.1	increased	increased
ClO_2	n/a	increased	increased
GAC	80.3	decreased	decreased

TABLE 3
Pilot Test Unit Description and Testing Conditions for Refinery B

Flow Velocity (gpm/ft^2)	4.2
Adsorber Diameter (ft)	4.0
Weight GAC/vessel (lbs)	2000
Average TOC (mg/l)	- (range 13-105)
Average COD (mg/l)	63
Average TSS (mg/l)	6 (range 2-45)

TABLE 4
Pilot Test Unit Description and Testing Conditions for Refinery C

Flow Velocity (gpm/ft^2)	5.4
Adsorber Diameter (ft)	0.125
Weight GAC/vessel (lbs)	0.45 (6 columns in series)
Average TOC (mg/l)	53
Average COD (mg/l)	162

TABLE 5
Pilot Test Unit Description and Testing Conditions for Chemical Plant A

Flow Velocity (gpm/ft^2)	2.39/3.18
Adsorber Diameter (ft)	4.0
Weight GAC/vessel (lbs)	2000
Average TC (mg/l)	95
Average TOC (mg/l)	48
Average TSS (mg/l)	25

TABLE 6
Treatment Costs for Toxicity Reduction Using GAC

Site	$/1000 gal
Refinery A	n/a
Refinery B	0.5
Refinery C	1.4
Chemical Plant A	1.4

Figure 1: Schematic of a systematic TRE.

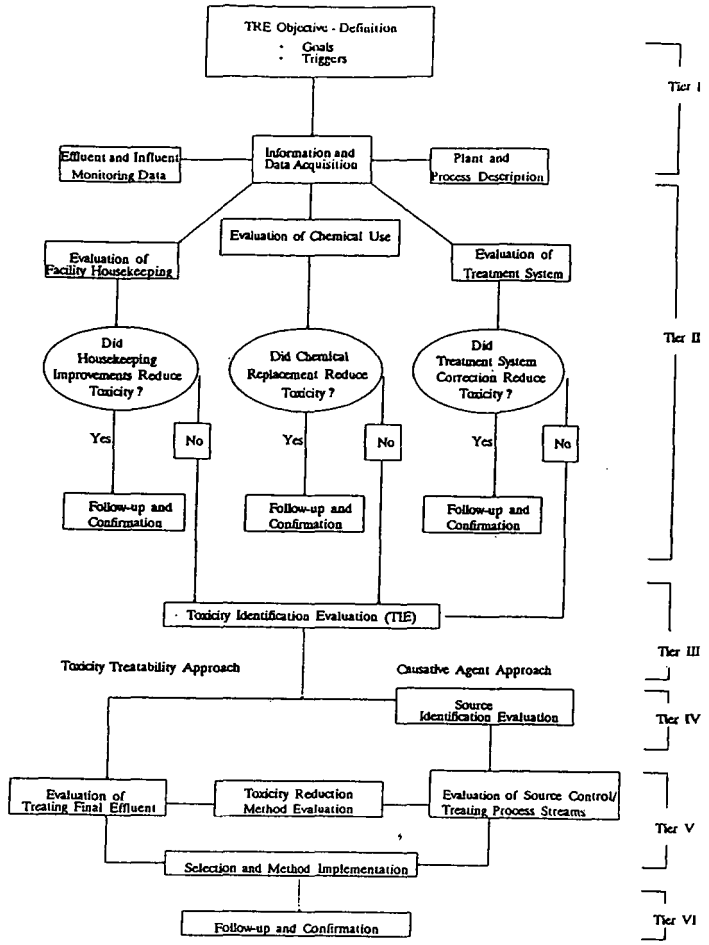


Figure 2: Toxicity data from the pilot study for Refinery B.

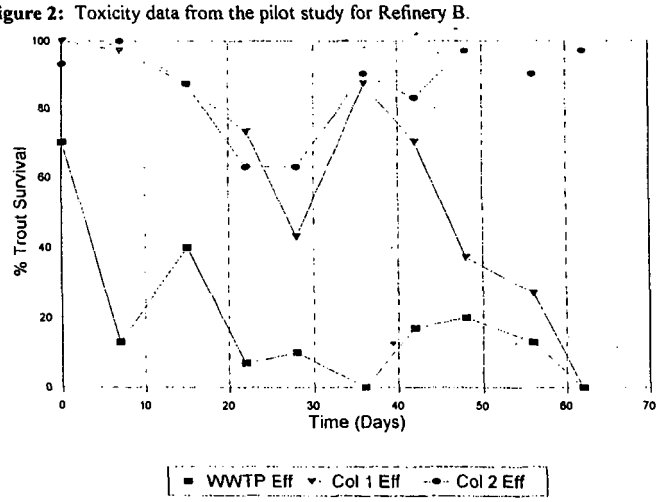


Figure 3: TOC breakthrough data with toxicity data superimposed for the Refinery C optimization study. Data for toxicity breakthrough from the commercial system is also included.

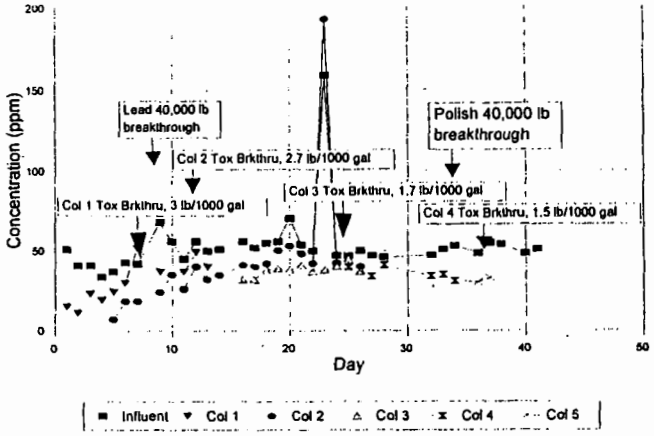


Figure 4: Daphnia toxicity data from the Chemical Plant A pilot study.

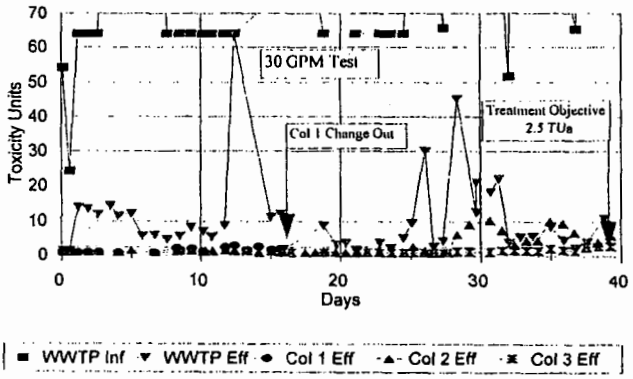
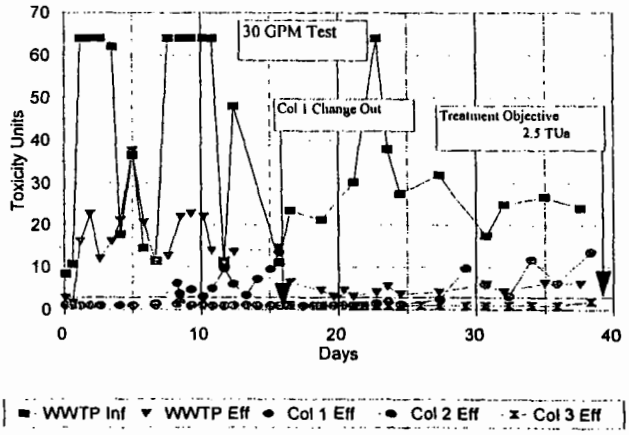


Figure 5: Fathead minnow toxicity data from the Chemical Plant A pilot study.



ADSORPTION OF HERBICIDES USING ACTIVATED CARBONS

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Keywords: activated carbon, water pollutants, herbicides

INTRODUCTION

This paper describes the results of research in which novel activated carbons have been examined for their efficacy in water treatment and, specifically, for the adsorption of a common herbicide and wood preservative, sodium pentachlorophenolate. To place this work in context, the introduction will discuss first some of the considerations of using activated carbons for water treatment, and then certain aspects of the authors' research that has led to this particular topic.

Activated Carbons for Water Treatment

One of the largest uses of activated carbons lies in the treatment of domestic and industrial water supplies. Activated carbons in various physical forms, have been used for more than 50 years to treat public water supplies for the removal of organic compounds that adversely affect taste, odor, and toxicity. Powdered activated carbons are used on a once-through basis, while granular activated carbons (GAC) possessing high surface areas, coupled with high attrition resistance, are used in packed bed applications.

Rising concern about the quality of drinking water supplies as well as the increased awareness of pollution from industrial waste waters have led to a significant growth in the activated carbon market. Demand for ion exchange resins and activated carbons for water treatment reached 200 million lb in 1992 and is expected to grow 4.6% per year to 251 million lb by 1997, mainly due to increased demand for activated carbons. The corresponding market value for these materials reached $271 million in 1992 and it is expected to rise to $376 million by 1997[1]. A small but ever-increasing market for activated carbons is also developing in the area of household water filtration systems for improving the quality of drinking water.

The surfaces of most commercial activated carbons are hydrophobic, which means that they are very effective for the adsorption of non-polar organic molecules. Activated carbons are less effective for the removal of polar compounds, and still less useful for the adsorption of ionic species (e.g. metals). For this reason, household treatment systems use activated carbon in multi-component filters that may also include materials such as ion-exchange resins. The high cost of ion-exchange media excludes their use in large-scale water treatment processes, where activated carbon is the preferred choice. However, there is a need to develop activated carbons that can be comparably effective for the adsorption of a wide range of pollutants.

Granular activated carbons have gradually replaced powdered activated carbons in water treatment and are now used on a much larger scale than ever before. In 1986 the Amendments to the Safe Drinking Water Act specified adsorption with GAC as the benchmark technology for organic chemical removal[2]. Alternative technologies must be at least as effective in controlling synthetic organic chemicals. Municipal water plants traditionally incorporate fixed beds of GAC as part of the filtration system, the carbon bed acting as a physical filter, as well as an adsorbent. The high attrition resistance of GAC is important to water treatment applications in that it allows for the carbons to be backwashed, pumped, excavated and recycled through regeneration units without suffering excessive material loss due to mechanical abrasion[3]. Although granular carbons are generally more expensive than powdered carbons, they have been found to be more cost-effective when their overall usage rate is high. Pressure drop, containment, and other considerations make powdered carbons impractical for use in adsorber beds.

Activated carbon fibers have recently started to attract interest as adsorbents for a number of applications, including water treatment[4]. Among other factors, the narrow fiber diameters (typically 10 to 30 microns) allow rapid rates of adsorption and desorption - a characteristic that also applies to fine particle powdered carbons. However, cost has so far presented one of the major obstacles to wide-scale development (over $20/Kg for carbonized fibers, i.e. before activation). In addition, to surmount problems in handling and utilization, it will be necessary to incorporate the fibers into some type of structure.

Current Research

Over the past few years, research at this Center has been involved with investigations of the synthesis of activated carbons by different methods and from a range of precursor materials[5-10]. The general objectives are to develop a basic understanding of the mechanisms leading to the formation of an extensive pore structure, and ultimately to be able to produce activated carbons with controlled porosity and surface chemistry, as well as other properties. These investigations have included: the formation of activated carbon particles and extrudates by the phosphoric acid activation of hardwoods and blends of hardwood with other materials [5,6]; activated carbon particles by the KOH activation of bituminous coals [7]; activated carbon extrudates by the KOH activation of lignite and oxidized bituminous coal [8]; activated carbon fibers from isotropic pitch precursors [9];

and the development of rigid, monolithic activated carbon composites [10].

The present work is related primarily to activated carbon composites. These are strong, highly permeable materials that can be produced in almost any size or shape, and are particularly suitable for applications where it is desirable to achieve high rates of throughput with minimum pressure drop. Moreover, the use of an immobilized bed can eliminate the attrition that would occur with a granular bed. Emanating from this work, we have found that it is possible to alter the pore structure of the activated carbon, and to introduce heteroatoms, such as nitrogen, into the structure by altering the method of synthesis. These attributes are germane to water treatment applications in two respects. First, the effectiveness of activated carbons in any particular application is dependent upon the pore size distribution: generally, for water treatment, a proportion of wider pores is desirable, both to facilitate diffusion of the adsorbate through the liquid phase, and to be able to accommodate large adsorbate molecules, such as color bodies and humic acids. Second, as already noted, activated carbons are typically hydrophobic. A number of studies has shown that the deliberate introduction of surface species, such as oxygen-containing groups, can enhance the ability to remove contaminants such as polar compounds and metals [11-13]. However, the necessary treatments can be expensive, and it is difficult to control the type and distribution of the surface groups. By the introduction of heteroatoms directly during the synthesis process, it should be possible to provide specific surface functionalities that are uniformly distributed over the adsorbent surface, and that may enhance the adsorptive capacities for non-polar species. In the research described here, we have conducted preliminary experiments to assess the potential of different formulations of activated carbon composites for the removal of a representative polar contaminant of groundwaters.

EXPERIMENTAL

In their original form, activated carbon composite materials have been prepared in collaboration with the Oak Ridge National Laboratory [10,14]. These composites are made from water slurries containing chopped carbonized pitch based fibers (~ 15 - 20 μm diameter x ~ 0.35 mm length, supplied by Ashland Carbon Fibers Division, Ashland Inc.) and a phenolic resin. The slurry is vacuum molded into tubular or plate configuration, followed by drying, curing and carbonization to 650°C. The composite is activated in steam or CO_2 at temperatures from 800-900°C to introduce porosity. The method of preparation of the other composites that have been prepared for this work is proprietary and will not be described here.

Some properties of the activated carbon composites are presented in Table 1, together with data for a commercial granular activated carbon that was used for comparison. Composite J was prepared by the method described above. It can be seen that these adsorbents possess quite different pore structures. The BET surface areas range from 660 to 1940 m^2g^{-1}, and have very different pore size distributions: some are predominantly microporous (pores < 2 nm diameter) and some have very high mesopore volumes (pores 2 - 50 nm diameter). The commercial water treatment carbon has a BET surface area at the low end of this range, but possesses an appreciable mesopore volume.

To measure the adsorptive capacities of the activated carbon composites for sodium pentachlorophenolate (PCP), 1.3 cm diameter plugs were cut from 1.5 cm blocks of activatedmonolith using a hole-saw. Three such plugs were lain end to end to form a column oftotal length 4.5 cm and volume 6 cm^3. The column was then sealed into a water-tight assembly using heat-shrink tubing (Markel Corporation, polyolefin tubing), by heating to approximately 180°C using a heat gun. The ends of the column were fitted with plastic barbed connections enabling Tygon tubing to be attached.

Comparable columns of granular activated carbon were prepared by sealing 2.0 g samples of carbon into polyolefin tubing, using the same technique, to create a column of volume 8 cm^3 and length 6 cm. Plugs of quartz wool were fitted at the column ends to contain the bed. A peristaltic pump, Pulsafeeder - Mec-o-matic VSP-20, located downstream of the column continuously drew a 40 ppm solution of sodium pentachlorophenolate (NaC_6Cl_5O) from a reservoir and through the column. The concentration of PCP in the column effluent stream was monitored via a UV-Vis spectrophotometer (Varian, Series 634) fitted with a 10 mm path length flow-through quartz cell, at a wavelength of 317.5 nm. Column breakthrough was determined as the point where the ratio of effluent to inlet PCP (C/Co) was equal to 0.3. The flow rate of PCP solution through each of the columns was held constant at 1 $ml.min^{-1}$.

RESULTS AND DISCUSSION

At the time of writing, adsorption data for PCP are available for the composite J and the commercial carbon. A plot of C/Co is shown as a function of the number of column volumes of PCP solution that have been processed in Figure 1. The breakthrough time for composite J was found to be almost 1400 column volumes, whereas it was closer to 150 column volumes for the granular carbon - a factor of about nine. It should also be noted that both columns continued to adsorb PCP after breakthrough and never reached saturation.

At first sight, the difference in the performance of these carbons is surprising, since they are of comparable surface area (see Table 1), and the commercial product has a much greater total pore volume (0.76 vs 0.39 cc/g) and, therefore, expected adsorption capacity. It is possible that part of

the difference may be attributable to the way in which the two columns are formed. As the activated composite is a monolith, the composition of the column is uniform over its cross section and length, and all of the solution has to pass through the interior of the composite before emerging: the monolithic form effectively ensures that the fluid feed is distributed uniformly through the column. With any granular bed, inefficiencies in packing can lead to channeling, allowing some of the feed to experience shorter contact times than the average that is calculated over the whole column: this phenomenon is more likely to occur in shallow packed beds.

At the same time, it is interesting to find that, at a similar overall space velocity (the volume feed rate per weight of carbon is 33.3 h^{-1} for the composite and 30.0 h^{-1} for the granular carbon), the column of composite is much more effective in adsorbing PCP. This observation indicates that the rate of adsorption is faster over the composite than the granules, which is consistent with other observations. The narrow diameter of the fibers (15 - 20 μm) essentially minimizes mass transfer limitations, and allows much faster rates of adsorption (and desorption) than is possible over large granules, as illustrated by an example obtained by a TGA study of the gas phase adsorption of NO, Figure 2. The rate of NO uptake is found to be higher by as much as three orders of magnitude for an activated carbon fiber composite than for 2 mm granules. Only when the granules are reduced to a size comparable to that of the fiber diameter, do the rates correspond. Thus, powdered carbons could be used with comparable effectiveness if the practical difficulties of containment, and the penalty of the pressure drop over a column of fine particles could be surmounted.

A second factor is that the composites have a very open architecture (approximately 90% is free volume), which means that the contacting fluid enjoys free access to the adsorbent surfaces. Essentially, the composite can be viewed metaphorically as a situation in which the granules have been "peeled open" to allow the adsorbent to readily access all of inner adsorbent surface, which can otherwise only be approached by diffusion through an extensive pore network.

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ACKNOWLEDGEMENTS

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Table 1: Properties of activated carbon adsorbents

Sample	BET surface area (m^2/g)	Pore volume (cc/g) micro	meso	Bulk Density (g/cc)
A	870	0.42	0.03	-
E	1140	0.43	0.87	-
F	1940	0.76	0.73	-
I	1930	0.61	1.10	-
J	790	0.38	0.01	0.30
Granular carbon*	660	0.29	0.47	0.25

* commercial water-treatment carbon, 1-2 mm granules

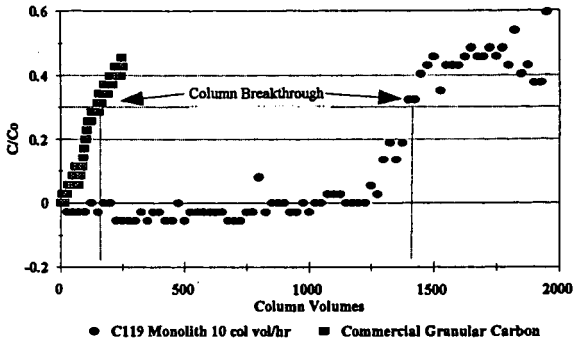

Fig. 1. Adsorption of Na-PCP by Carbon Columns

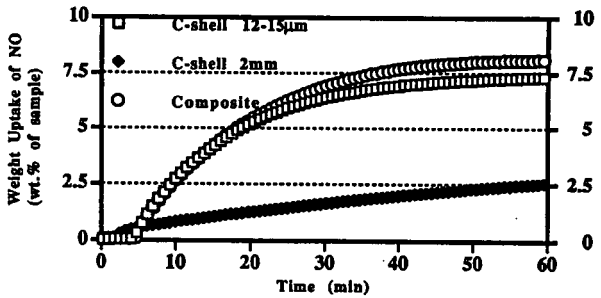

Figure 2: Adsorption rate of NO on activated carbon composite compared with a commercial granular activated carbon at two average particle sizes; 2mm, and finely ground to 14μm.
(c-shell= coconut shell)

CARBONIZED MATERIAL ADSORBENTS FOR THE REMOVAL OF MERCURY FROM AQUEOUS SOLUTIONS

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Keywords: adsorption, carbonized materials, mercuric chloride

Introduction

Although wood has essentially been excluded as a starting material for the production of granular activated carbon because of the poor strength and friability of the products [1], powdered wood based activated carbons are still being used in water treatment and other liquid phase applications. However, the capability of powdered wood-based charcoal which in itself porous has not been fully known. Few studies have been conducted in harnessing its potential for adsorption purposes especially in water treatment.

This study was conducted to investigate the possibility of using wood based carbonized materials from Sugi (Cryptomeria japonica D. Don) as adsorption materials in aqueous solutions of heavy metals like mercury, zinc, lead, cadmium and arsenic. However, of all the heavy metals investigated, mercury is considered to be the most toxic so this paper describes only the adsorption ability of the carbonized materials in adsorbing this metal from aqueous solutions of different concentrations.

Materials and Methods

A. Materials

The raw materials used in this study were Sugi , activated carbon from coconut shell and Mercuric chloride ($HgCl_2$) as heavy metal.

B. Methods

1. Preparation of Materials: Small diameter logs of Sugi were cut into flakes and made into powder. Wood powder was passed through a 20-mesh size sieve. The wood powder was ovendried at 105± 2 °C prior to carbonization.

2. Carbonization Process: Wood powder was carbonized in a furnace with the desired temperatures of 200, 400, 600, and 1000 °C. Nitrogen (N_2) gas of 1500 ml/min. was flowed in a heating rate of 4 °C/min. After getting the desired temperature, it was kept for one hour and then turned it off. The charcoal was cooled naturally before it was taken out of the furnace.

3. Adsorption Experiment: Aqueous solutions of 5, 50 & 100 ppm $HgCl_2$ were prepared. Each of the carbonized materials with a weight of 0.5 g was mixed with 50-ml $HgCl_2$ solution and continuously stirred in a hotting bath at 30± 2 °C for 1, 4, 8 and 24 hours of soaking time. The mixtures were filtered with ADVANTEC Toyo glass fiber filter paper. The concentration of the filtered solution was determined using an Inductively Coupled Plasma machine.

4. Determination of Acidity and Dissolved Oxygen of the Solute: The acidity of the solution was measured using a pH meter while that of the dissolved oxygen was measured using a COD meter.

Results and Discussion

1. Adsorption ability of carbonized wood materials

Figures 1-3 show the relationship between total soaking time and adsorption of carbonized materials. Based from Fig. 1, similar adsorption behavior was observed in all the carbonized materials. The adsorption was highest in 1000 °C in all the total soaking times, and then followed by 600 °C and 200 °C. It can be observed that the adsorption in activated carbon is not comparable with the high temperature carbonized materials. Further, adsorption in 1000 °C was almost the same in all the total soaking times.

In Fig.2, adsorption was still highest in 1000 °C in all the soaking times and then followed by 600 °C and activated carbon. However, it can be observed that 105 °C and 200 °C had a remarkable adsorption compared when soaked at 5 ppm solution and even comparable with the high carbonized materials (8 & 24 hours).

Different results were observed in 100 ppm solution (Fig.3). Although the adsorption trend of all the carbonized materials in all the total soaking hours was the same with that of 5 and 50 ppm, it can be observed that at higher concentrations of $HgCl_2$ solution, higher adsorption is observed not only at 1000 °C but also in activated carbon. Moreover, it can be noticed that activated carbon adsorbed almost the same as the high carbonized materials unlike in the low concentrations.

Generally, the extent of adsorption depends mainly on the surface area and the chemical nature of the adsorbents.[2] Based from the preliminary measurement of the specific surface area of the adsorbents, high carbonized materials have higher specific surface areas. However, in this study, it is clear that surface area was independent of the adsorption. The higher temperature carbonized materials with a high specific surface area performed almost the same with the low temperature materials. The chemical properties which can be a source of explanation on certain extent seem not to have any effect especially on lower concentrations of $HgCl_2$ solutions. The elemental analysis results of the carbonized materials [3] revealed that the carbon contents increases with the increase of temperatures. Consequently, carbonized materials with high carbon content adsorbs more than those with low carbon content materials. However, in higher concentrations of $HgCl_2$, higher carbonized materials adsorbs more than those of low carbonized materials.

According to Lee, et al.[4], in general, adsorption capacity can be influenced both by the microspore structure and also by the surface chemistry interactions. Carbon surfaces are covered with chemisorbed oxygen species which have a profound influence on surface properties.[5] In a study conducted on the removal of chromium (metal) from aqueous solutions by activated carbon adsorbents, it has been observed that not only the microporous structures and the surface area but the chemical structure of the carbon surface plays an important role in the adsorption. In particular, the nature of the surface-oxygen chemical structure present in the carbon surface, not the total amount of oxygen determines the adsorption of chromium. [6] The addition of oxygen-containing functional groups to the carbon surface caused by the exposure in the atmospheric thus altering its adsorptive properties [7] is a probable source of change in the surface oxygen chemical structure which in turn affects its adsorption capability.

In another study conducted on the lightest metal, Lithium(Li), diffusion is the main parameter in controlling the adsorption of this metal. Interaction of Li with surface groups may also play an important role in the adsorption process. [8]

2. Water purification ability of carbonized materials

In connection with the pollution of water, the content of dissolved oxygen in water is of prime concern. The overuse of water systems for disposal purposes in many instances had almost fully depleted the dissolved oxygen available for life support.

In this study, the amount of COD was monitored with soaking time. Table 1 shows the decrease in the amount of COD of the $HgCl_2$ solution

after 24 hours of soaking the carbonized materials. Rate of decrease is somewhat higher for the high carbonized materials and activated carbon. The decrease in the COD values through time can be observed through a sample graph as shown in Fig.7.

The pH values after treating the carbonized materials in 24 hours is shown in Table 2. The original $HgCl_2$ solutions which was acidic was made close to neutral or neutral for 600 °C and 1000 °C, and activated carbon after it was treated with carbonized materials. However, at 105 °C and 200 °C, the pH values also increased but at low concentrations only. Fig. 9 shows the behavior of pH value with total soaking time.

Conclusion

Wood based carbonized materials can be used as adsorption materials in treating aqueous solutions of heavy metals like mercury. However, the behaviour of the adsorption of carbonized materials in $HgCl_2$ solutions cannot still fully explained because of lack of basic information on the nature of the adsorbent materials. Microporous structure and surface-oxygen chemical structure present in the carbon surface will be investigated in future studies to further explain the adsorption ability of this heavy metal.

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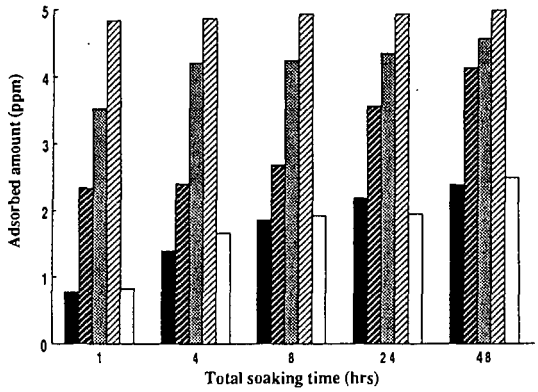

Fig. 1. Relationship between total soaking time and adsorbed amount of HgCl in 5 ppm aqueous solution.

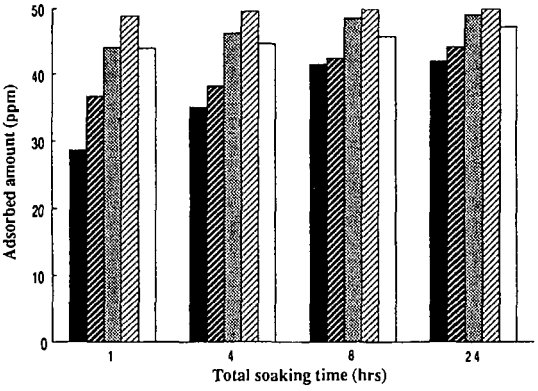

Fig. 2. Relationship between total soaking time and adsorbed amount of HgCl in 50 ppm aqueous solution.

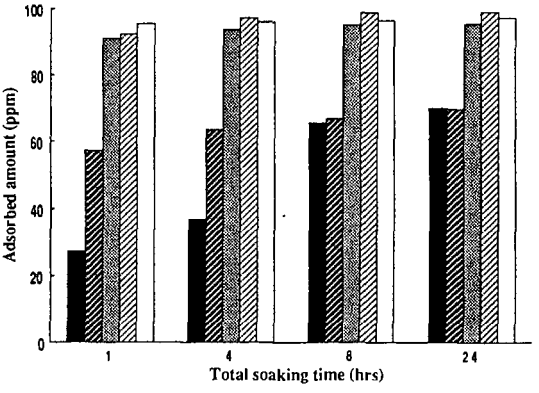

Fig. 3. Relationship between total soaking time and adsorbed amount of HgCl in 100 ppm aqueous solution.

Legend: ■ Control
▨ 200°C
▩ 600°C
▨ 1000°C
□ Activated charcoal

Note: Control - wood powder ovendried at 105°C

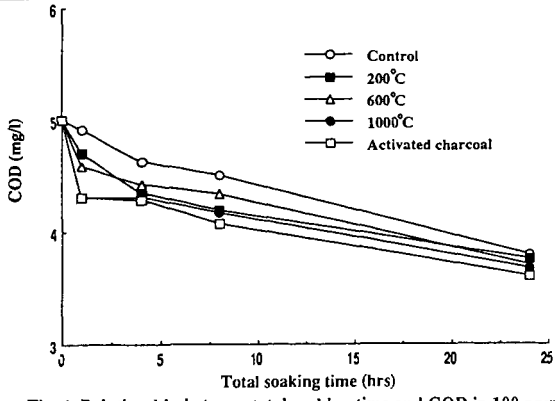

Fig. 4. Relationship between total soaking time and COD in 100 ppm aqueous solution.

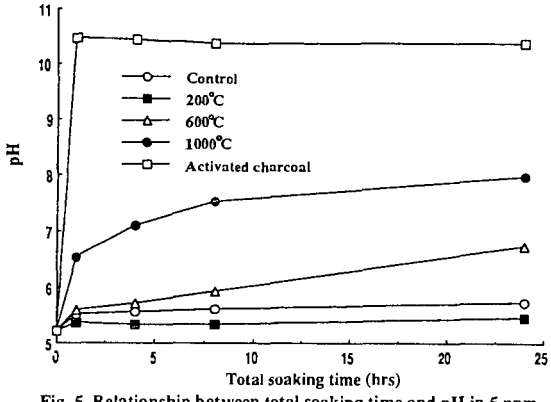

Fig. 5. Relationship between total soaking time and pH in 5 ppm aqueous solution.

Table 1. Effects of carbonized materials on the COD of $HGCl_2$ aqueous solutions after 24 hours.

	COD (mg/l)			Rate of decrease (%)		
	1	2	3	1	2	3
Original $HgCl_2$ solution	5.600	5.050	5.000	-	-	-
Carbonized materials						
Control	3.570	3.650	3.790	36	28	24
200 °C	3.520	3.620	3.750	38	28	25
600 °C	3.460	3.600	3.100	38	29	38
1000 °C	3.460	3.500	3.070	38	31	39
Activated charcoal	3.390	3.450	3.000	39	32	40

Legend: 1 - 5 ppm; 2 - 50 ppm; 3 - 100 ppm

Table 2. pH values of $HgCl_2$ aqueous solutions treated with carbonized materials after 24 hours.

	pH		
	1	2	3
Original $HgCl_2$ solution	5.21	4.92	5.23
Carbonized materials			
Control	5.72	5.12	4.45
200 °C	5.45	4.88	4.69
600 °C	6.73	5.98	5.79
1000 °C	7.96	7.56	7.34
Activated charcoal	10.35	9.60	9.11

Legend: same as in Table 1.

THE ION EXCHANGE PROPERTIES OF LOW RANK COALS ON ACTINIDES AND OTHER HEAVY METALS

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Keywords: actinides, ion exchange, lignite

ABSTRACT

The removal of heavy metal and low-level radioactive wastes from the environment and their subsequent immobilization in an appropriate repository is one of the major environmental challenges facing our nation. The scope and magnitude of the contamination at many DOE and Superfund sites are such that successful remediation will require the development of new, inexpensive technologies which remove, in an environmentally acceptable manner, the heavy metal and radioactive wastes from contaminated soil and water. In this paper, we will present the preliminary data on the viability of using low rank coals or lignites as a novel, inexpensive material to remove actinides and other metals from the aqueous system, and the effects of high radiation on ion-exchange properties of lignites.

INTRODUCTION

After more than a half a century of nuclear processing activities by DOE and its predecessors, a wide range of wastes and environmental problems exists at more than 100 contaminated installations in 36 states and territories.(1) Uncontained hazardous and radioactive contaminations in soil and ground water exist throughout the DOE complex. The calls for developing cost-effective technologies to remove radioactive and toxic metal contaminants from the waste processing streams and ground water, and to reduce secondary waste volumes are the top priority for environmental restoration at the DOE sites.

In groundwater, the most common binary contaminant found in the DOE sites is a mixture of radionuclides, metals, and chlorinated hydrocarbons. The most important metal contaminants identified are lead, chromium, arsenic and zinc; radionuclide contaminants are tritium, uranium, strontium, plutonium, cesium, cobalt, technetium, and iodine.(2) At the Waste Treatment Facility at Los Alamos National Laboratory (LANL) and Rocky Flat Plant (RFP), the principle metal contaminants found in these processing streams are plutonium (Pu) and americium (Am). Waste water streams generated from the research operations, reactors, and radiochemical production facilities such as Savannah River Site, Oak Ridge Y-12 Plant, Fernald Plants, and Hanford Site contain a wide spectrum of radionuclides (e.g., strontium, cesium, technetium, nickel, uranium, thorium, and radium), heavy metals, reactive chemicals, and organic solvents.(1)

Clearly the scope and magnitude of the contaminations at various DOE sites require the development of new, inexpensive technologies which would remove, in an environmentally acceptable manner, the heavy metal and radioactive wastes from contaminated soil and water. Conventional treatments of radioactive waste water at the DOE sites are the precipitation methods, which generate large volumes of secondary radioactive sludge waste. The other common technologies for removal of heavy metals from ground water and waste water are ion exchange resin based processes; however, these commercial resins are usually very costly (> $10/lb) and generate secondary acid waste from the regeneration process.

In the past few years, the University of Kentucky Center for Applied Energy Research (CAER) and Department of Chemistry have developed a system based on the unique ion exchange properties of low rank coals for the treatment of large volumes of water containing low to moderate levels of metal contaminations.(3),(4),(5) Because of the cationic selectivity of lignites

on a high charge density metal, a collaborative effort between the University of Kentucky and Inorganic Elemental Analysis group (CST-8) at LANL will attempt to address the needs of DOE environmental cleanup of actinides and other heavy metals from the aqueous system, and reduce the generation of secondary sludge waste from the waste water treatment process. Our goals are (1) to develop a novel, inexpensive material to remove actinides (Pu, Np, Am, and U) and heavy metals from the waste water streams and ground waters, (2) to understand the ion exchange mechanism of actinides with low rank coals, and (3) to study the effect of radiation on ion exchange properties of lignites.

ION-EXCHANGE PROPERTIES OF LIGNITES

Low rank coals, brown coals or lignites are characterized by low specific energy, high oxygen and moisture contents and poor internal strength (the latter excludes underground winning of low rank coals). The high moisture content of the coal retards efficient combustion and must be removed by energy consuming processes prior to combustion. An economical use of brown coal for power generation is feasible only when the combustion process is located close to the coal supply, minimizing the amount of transport required between coal source and power station. The high oxygen contents of low rank coal does however impart one unique property to these coals, that of the ability to remove cations from solution via ion exchange with carboxylic acid and phenolic hydroxyl functional groups on the coal surface. These functional groups undergo dissociation in solution to form a negatively charged site upon the coal surface which is subsequently capable of complexing cationic species from solution to form a stabilized coal-metal structure. The dominant functional group responsible for the ion exchange process has been shown to be the carboxylic acid group. These weak acid sites are virtually completely dissociated at solution pH's greater than 4, and would therefore be ideal for the treatment of most natural water samples which routinely display pH values between 4 and 9. The coal however, would not be suitable for treating many industrial waste streams which have pH values often less than 1. Slight adjustment of pH to the waste streams may be required.

Table I gives the typical cation exchange capacities of various North American lignites. The cation exchange capacities of these coals are considerable lower than those measured for commercially available synthetic ion exchange resins (~ 0.4-1.0 meq/g c.f. 7-10 meq/g for commercial resins) however the lower cost of the coal (~ $10/ton) compared to the commercial resins (~$10/lb) makes the cost per unit volume of solution treated significantly lower for the coal based process. Table II shows the calculated cost per liter for both a brown coal and synthetic resin based process treating several different 100 ppm solutions. The processing costs listed in Table II show that the lignite based process is cheaper than a resin based system by a factor of 170, although the total mass of adsorbent used in the coal based process is 18 times that of the resin. However, for the proposed solutions to be treated, e.g. groundwater containing low to moderate levels of contamination, processing costs are envisaged to be the main criteria in determining which process would be used, and would therefore favor the implementation of a coal based system.

TABLE I. Cation Exchange Capacities (meq/g) measured for North American Lignites (1000 ppm solution, 5 g coal/100 mL solution)

Metal	West Kentucky	North Dakota	East Texas
Cd	.35	.38	.37
Pb	.20	.22	.21
U	.16	.17	.17
Hg	-	.22	

TABLE II. Cost per Liter (cents) to treat 100 ppm Solution of Divalent Metal. Using Brown Coal and Resin Based Systems

Metal	Brown Coal @ $10/ton 0.4 meq.g^{-1}.	Ion Exchange Resin @ $30/kg 7.0 meq.g^{-1}.
Cu^{2+}	7.88×10^{-3}	1.351
Cd^{2+}	4.44×10^{-3}	0.763
Hg^{2+}	2.49×10^{-3}	0.427
U^{2+}	2.10×10^{-3}	0.360

APPROACH

A series of standard adsorption experiments, principally in batch mode, will be conducted on the Western Kentucky lignites with solutions containing actinides (e.g., ^{239}Pu, ^{241}Am, ^{237}Np, and ^{234}U). Some of the key variables that are known to effect lignite exchange capacity, which will be investigated as initial part of the study include:

- Cation exchange capacity as a function of solution pH.
- Cation competition effects.
- Effect of multiple low loading contacts compared to single high loading contacts.

Quantitation of radionuclide adsorption will be performed using a combination of liquid scintillation and alpha spectroscopy. The experiment will be conducted in a wide range of radioactivity (from several hundred pCi/L to mCi/L level) in order to simulate the radioactive contaminants present in the ground water to the waste processing streams.

In addition to adsorption study, a sample of Western Kentucky lignites is currently exposed to a ~ 2.5 rem per hour gamma-radiation source (radiation dose = ~2.5 rads per hour). We plan to expose this sample to the radiation source with several thousand rads (> 2 months) and examine the structure of functional groups in the lignites after irradiation. This will give us some opportunities to compare the ion exchange capacities of lignites before and after exposing to relatively high radiation field.

EXPECTED RESULTS

The analytical results from the proposed experiment are not available at the time of publication. From the previous work,[3],[4],[5] a single 5% loading w/v (2.5 grams of coal dry weight per 50 mL of solution) of Western Kentucky and East Texas lignite removed greater than 99% of the uranium from a 1000 ppm uranium (uranyl nitrate) solution. We anticipate that the other highly charged actinide species (Pu, Am, Np) will interact with lignites similar to uranium in the aqueous system.

CONCLUSION

The success of developing a system, which utilizes low-rank coals as an ion-exchange media for removals of radionuclides and heavy metals in environmental cleanup and waste water treatment, would dramatically reduce the cost of expensive environmental remediation and industrial waste stream treatments.

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THE USE OF CARBON AEROGEL ELECTRODES FOR ENVIRONMENTAL CLEANUP

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Keywords: carbon aerogel electrodes, deionization of water, heavy metal removal from water

INTRODUCTION

An electrochemical cell with a stack of carbon aerogel electrodes has been used to remove a variety of contaminants from aqueous waste streams and natural waters. In the case of non-reducible and non-oxidizable salt solutions, the cell is operated in a capacitive mode [1-7]. Electrolytic or electrophoretic deposition is used for the removal of heavy metals. The removal of $NaNO_3$ from water with subsequent concentration is an example of capacitive operation. Electrodialysis with bipolar membranes can be used to separate neutral salt solutions into their acid and base components so that recycle is possible, thereby lowering risk to the environment [8]. However, the electrodialysis process is not 100% efficient and generates a dilute waste stream of $NaNO_3$ in addition to the HNO_3 and NaOH product streams. Carbon aerogel electrodes can be used to remove $NaNO_3$ from the effluent, concentrating it for recycle to the electrodialysis cell. Solutions are passed through a stack of carbon aerogel electrodes, each having a very high specific surface area (400 to 1100 $m^2\ g^{-1}$) and very low electrical resistivity (less than 40 mΩ-cm). After polarization, Na^+ cations and NO_3^- anions are removed from the electrolyte by the imposed electric field and held in electric double layers formed at the surfaces of electrodes. Two streams are produced, pure water and $NaNO_3$ concentrate. This process is also capable of removing other impurities such as dissolved heavy metals and suspended colloids. In these cases, contaminants are removed by electrodeposition and electrophoresis, respectively. The carbon aeorgel cell has been used for the separation of copper, zinc, cadmium, and lead from 0.1 M KNO_3 solutions, as well as for the separation of cobalt, chromium, manganese, lead, and uranium from sea water. Treatability tests on ground water at LLNL have shown that chromium contamination can be reduced from 32 to 2 ppb, well below the acceptable level of 11 ppb. Previously, other types of porous carbon electrodes have been used for the removal of heavy metals from water. These electrolytic separation processes have several potential advantages over other more conventional technologies. Unlike ion exchange, no acids, bases, or salt solutions are required for regeneration of the system. Regeneration is accomplished by either electrical discharge or reverse polarization. Therefore, no secondary waste is generated. In contrast to thermal processes such as evaporation, such processes are more energy efficient. Since no high pressure pumps are required, these electrolytic separation processes offer operational advantages over reverse osmosis (RO).

ELECTROCHEMICAL CELL WITH CARBON AEROGEL ELECTRODES

A typical double-sided electrode is made by gluing two sheets of a carbon aerogel composite (CAC) to both sides of a titanium plate that serves as both a current collector and a structural support for the CAC. Conductive silver epoxy is used for gluing. Carbon aerogels were developed at Lawrence Livermore National Laboratory and are synthesized by the polycondensation of resorcinol and formaldehyde in a slightly basic medium, followed by supercritical drying and pyrolysis in an inert atmosphere. Sheets of CAC are made by impregnating carbon cloth with the resorcinol-formaldehyde solution and then carbonizing. This fabrication process results in unique open-cell carbon foams that have high specific surface areas (400 to 1100 $m^2\ g^{-1}$), optimal pore sizes (~50 nm), and a monolithic structure composed of interconnected colloidal-like particles or fibrous chains with characteristic diameters of 10 nm. This structure results in exceptionally low electrical resistivity (40 mΩ-cm). The porosity and surface area of aerogels can be controlled over a broad range, while the pore size and particle size can be tailored at the nanometer scale. Each sheet of CAC used in the experiments described here is 6.86 cm x 6.86 cm x 0.0125 cm, has a total active surface of approximately 2.8×10^6 cm^2, and a through resistance of about 10 $\mu\Omega$. Two orifices are located along one side of the carbon aerogel electrode and admit water to the electrode gap. A pattern of holes are located around the perimeter of the titanium plate and accommodate 12 threaded rods that hold the cell stack together. Even electrodes serve as cathodes while odd electrodes serve as anodes. The electrodes and headers are aligned by the threaded rods. An electrode separation of 0.05 cm is maintained by cylindrical nylon spacers concentric with the threaded rods and a rubber

compression seal. Since the orifices in each electrode alternate from one side of the stack to the other, the flow path through the stack is serpentine. Flow through the cell is generated by a programmable, magnetically-coupled, screw pump with a 304 stainless steel head. The maximum flow rate that can be achieved with this pump is 3.5 L/min. The differential pressure across a stack of 48 electrodes is only 5 psi at a flow rate of 1.7 L/min. All lines are made of Teflon and have a nominal diameter of 1/4 inch. The cells are polarized by programmable power supplies that have a voltage range of 0 to 12 V or a current range of 0 to 60 A. Sensors are placed on the inlet and outlet lines of the cell. Electrical conductivity, pH, individual ion concentrations, and temperature are continuously monitored. A computerized data acquisition system logs important operating parameters such as voltage, current, conductivity, pH, and temperature. Data acquisition system is based on an Intel 486DX-33 microprocessor, a National Instruments 8-channel A/D converter, and LabTech Notebook data acquisition software for Microsoft Windows. X-ray fluorescence is used off line for the quantitative measurement of heavy metals.

REMOVAL OF NITRATE SALTS

The removal $NaNO_3$ from a fixed 4000 ml volume of water by a stack of 192 carbon aerogel electrodes is illustrated by Fig. 1. The circulation rate through the stack was approximately 1000 ml/min. After application of a voltage between two adjacent electrodes, Na^+ cations and NO_3^- anions are drawn towards the cathode and anode, respectively. These ions are held in the electric double layers formed at the extensive surface of the carbon aerogel electrodes until the voltage is reduced. Tests demonstrated that CDI with carbon aerogel can effectively remove $NaNO_3$ from water. Deionization was accomplished during charging, while regeneration was accomplished during discharge. The concentration and conductivity was cycled up and down numerous times by charging and discharging the stack. The ability of the CAC electrodes to remove ions from water, i.e., the electrosorption capacity, had a strong dependence on cell voltage. The best results were achieved at 1.2 V, with relatively poor performance below 0.6 V. During experiments without recycle, a characteristic breakthrough curve (not shown) was observed. Deionization of more concentrated solutions requires more carbon aerogel electrodes.

REMOVAL OF HEAVY METALS

Two carbon aerogel electrodes polarized at 1.2 V can remove copper, zinc, cadmium, and lead from a fixed, 500 ml volume of a 0.1 M KNO_3 solution (Fig. 2). The electrolyte was circulated through the electrochemical cell at a rate of 50 ml/min. The concentration of lead dropped from an initial level of approximately 1 ppm to less than 0.2 ppm after 4 hours of polarization. The concentration of copper dropped from 1 ppm to less than 0.05 ppm. At such low concentrations, one would expect rates of removal to be mass transfer controlled, similar in magnitude, and independent of the standard electrode potentials of the ions being deposited. However, the rates for several of the ions appear to be correlated to some extent with their standard electrode potentials, indicating that process efficiency may not be governed by mass transport alone. Forty carbon aerogel electrodes polarized at 1.2 V were able to remove trace quantities of cobalt, chromium, manganese, lead, and uranium from a fixed, 1000 ml volume of sea water (Fig. 3). Here too the electrolyte was circulated through the electrochemical cell at a rate of 50 ml/min. The initial concentration of each contaminant was 100 ppb. After 5 hours of polarization, the concentrations of cobalt, chromium, manganese, and uranium dropped to levels of about 5 ppb or less. The concentration of lead dropped to about 15 ppb. The slow increases in concentration observed between 5 and 25 hours are probably due to some combination of redissolution and particle entrainment. Such difficulties can be avoided by periodic regeneration of the carbon aerogel electrodes. No electrode separator was used in the experiments represented by Figs. 2 and 3. By incorporating an anion exchange membrane between anodes and cathodes, electrode regeneration by stripping is possible.

SUMMARY

In summary, it has been shown that capacitive deionization with carbon aerogel electrodes can be used to remove salts such as $NaNO_3$ from water. It has also been shown that electrolysis with carbon aerogel electrodes can be used to effectively remove a variety of heavy metals from process streams and natural waters. The exceptionally low electrical resistivity of the monolithic carbon aerogel electrodes, due to their unique interconnected nanostructure, has made it possible to eliminate metal substrates such as titanium in more recent cell designs. Recent cell designs use only carbon aerogel and a plastic such as polycarbonate. Disposable cells made of carbon aerogel and plastic are now being made and operated.

ACKNOWLEDGMENTS

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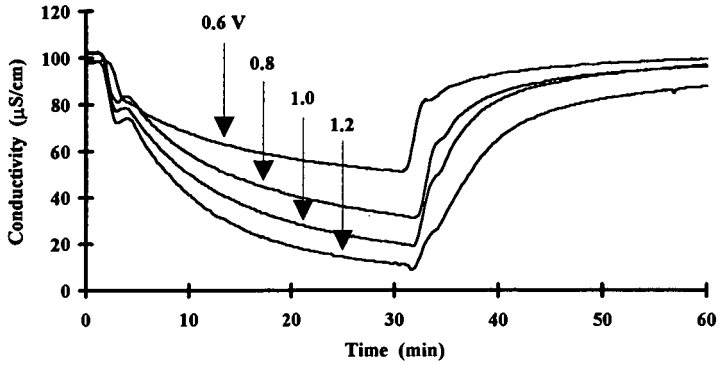

Fig. 1. Use of carbon aerogel electrodes in capacitive mode to remove $NaNO_3$ from fixed volume of electrolyte.

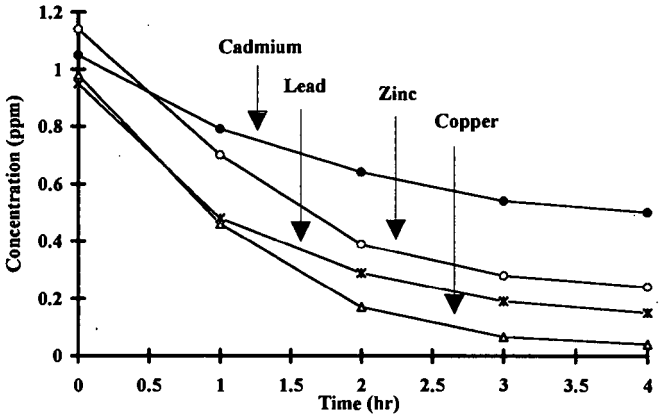

Fig. 2. Use of two carbon aerogel electrodes polarized at 1.2 V to remove copper, zinc, cadmium, and lead from a fixed 500 ml volume of a 0.1 M KNO_3 solution.

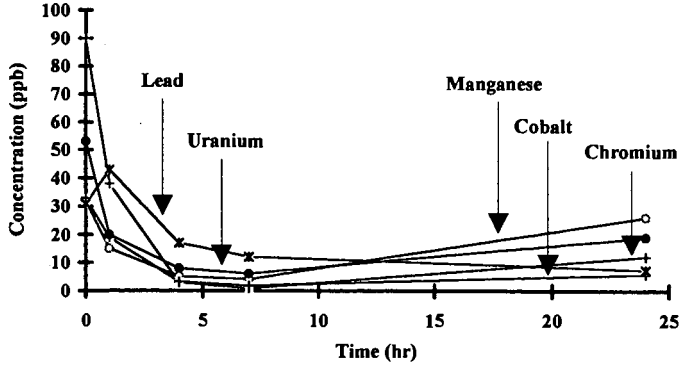

Fig. 3. Use of forty carbon aerogel electrodes polarized at 1.2 V to remove cobalt, chromium, manganese, lead, and uranium from fixed 1000 ml volume of sea water.

ENVIRONMENTAL POLLUTION CONTROL DEVICES BASED ON NOVEL FORMS OF CARBON

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Keywords: Electrochemistry, Trace Metals, Remediation.

Introduction

The purpose of this research was to assess the feasibility of using carbon devices for the electrochemical removal of heavy metal contaminants from aqueous streams. The ability of several carbonaceous materials to remove metal ions was evaluated using a porous flow-through electrochemical cell. The resulting effluent was monitored downstream using Anodic Stripping Voltammetry (ASV) to determine the decrease in analyte concentration and hence the electrode efficiency.

A schematic diagram of the apparatus used to carry out these experiments is shown in Figure 1. It is a two-cell system. The upstream working cell removes metal ions from the flowing stream, and the downstream analytical cell is used to measure the metal ion concentration in the resulting effluent.

The upper cell is used to test the various carbonaceous electrode materials for their ability to remove certain heavy metal ions from an aqueous stream. The cylindrical body is made of Lexan™. A solution flow channel is drilled through the Lexan™ body. The carbonaceous working electrode material to be tested is placed in the flow channel.

The analyte solution is pumped into the upper working cell and through the carbonaceous working electrode material. A peristaltic pump is used to control the flow rate for all experiments. For the cathodic removal of metal ions, a potential more negative than the standard reduction potential of the metal ion of interest is applied to the working electrode. This applied potential forces the plating of the metals onto the electrode surface thus removing the contaminants from solution. Various carbonaceous materials were obtained to assess their ability to operate as the cathode material. Reticulated Vitreous Carbon (RVC), a graphite fiber mat, a graphite felt and a proprietary carbon material were analyzed. The surface area of these materials was increased via a proprietary alteration technique. This increased surface area improves the ability of the carbon to remove metal ions from solution. Experimental parameters require optimization to maximize the removal of these metals. These parameters include pH, buffer concentration, solution flow rate, applied potential and carbon bed thickness. Conversion efficiency, long-term stability and loading capacity require appraisal. Finally, the pressure drop through the cell and flow characteristics of the solution flowing through the upper cell also need to be evaluated.

EXPERIMENTAL

The surface areas of the carbonaceous samples have been determined and the data are shown in Table 1. These surface areas were obtained using a Gemini III 2375 Surface Area Analyzer (Micrometrics Instrument Corporation, Nocross, GA). Standard operating procedures were followed as outlined in the operator's manual.

The cylindrical body of the upstream metal removal cell was made of Lexan™ (5.0 cm diameter, 6.0 cm length). The flow channel (1.6 cm i.d.) was drilled through the Lexan™ body. The Ag/AgCl reference electrode (3M NaCl, Model RE-4, BioAnalytical Systems, Inc. (BAS), West Lafayette, IN) was introduced into the flow channel through a Lexan™ sleeve positioned 90 degrees to the flow channel. Leakage was prevented using an o-ring and compression fitting. A piece of coiled platinum wire at the outlet of the cell was used as the auxiliary electrode. Contact to the working electrode was established via a platinum mesh positioned through the cell wall and sealed with an o-ring. The potential of the flow-through cell was controlled using a BAS Model PWR-3 Power Module.

The downstream, thin-layer flow cell (Model LC-44-01000, BAS) was used to measure the metal ion concentration before and after the solution is passed through the metal removal cell. The working electrode was a glassy carbon disk (0.3 cm diameter) over which the solution flowed. Two 50 μm spacers were used to produce the flow channel and direct the solution flow across the carbon disk. Prior to use, the glassy carbon disk was polished using successive slurries of 1.0, 0.3, and 0.05 μm alumina until a mirror-like surface was obtained. The glassy carbon electrode was then thoroughly washed with deionized water. A thin mercury film was plated onto the glassy carbon surface. The metal ions to be analyzed were accumulated into the mercury film. Following accumulation, the metal ions were electrochemically stripped from the mercury film and the measured current used to calculate the metal ion concentration. All potentials were measured relative to the Ag/AgCl reference electrode (BAS). Stripping voltammograms at the thin-layer flow cell were obtained using the

BAS Model CV-27 Voltammograph in conjunction with a Hewlett Packard Model 7044B X-Y recorder.

Stock solutions of metal ions were prepared using AA standard solutions (Fisher Scientific, Fair Lawn, NJ) and deionized water. The deionized water was further purified using a NANOpure™ ultrapure water purification system (Barnstead/Thermolyne, Dubuque, IA). These solutions were stored in Nalgene™ containers to avoid contamination. The $1X10^{-4}$ M Hg(II) solution for mercury plating was prepared from $Hg(NO_3)_2$ as needed. The mercury ion solution and sample solutions were prepared in 0.1M KNO_3 supporting electrolyte. The pH was adjusted to 3.5 using nitric acid. All chemicals were certified ACS grade purchased from Fisher Scientific unless otherwise noted.

PROCEDURE

The carbon material to be studied was pretreated to oxidize it and assist in the wetting of the carbonaceous surface. This was accomplished by placing the carbon material in a dilute solution (10%) of nitric acid over night in a covered beaker. The material was then thoroughly washed using deionized water. The carbonaceous material was then positioned into the metal removal cell. A threaded plug was used to press the material between a platinum mesh and a piece of filter paper. The pressure on the carbonaceous material can be easily adjusted by turning the threaded plug. This was important because it established contact between the carbon cathode material and the platinum mesh. A 0.1M KNO_3 electrolyte solution was pumped through the cell. In order to remove air bubbles and wet the electrode surface, a mild electrochemical pretreatment was used. The cell potential was held at +1.00 V for 10 minutes followed by -1.00 V for 10 minutes. The performance of the carbonaceous material under study was tested by placing a solution containing a known concentration of metal ion into the sample reservoir. The solution was then allowed to pass through the metal removal cell at a known flow rate and applied potential. The performance was assessed by measuring the metal ion concentration in the effluent and comparing it to the initial ion concentration. The percentage efficiency of the cell is equal to the percentage of metal ions removed from the solution by the electrolytic cell.

A pre-plated mercury film was used for downstream anodic stripping voltammetric (ASV) detection of the metal ion in the effluent stream. A $1X10^{-4}$ M Hg(II) solution in 0.1M KNO_3 was purged with nitrogen for 20 minutes to remove any oxygen. The mercury film was produced by applying a potential of -1.00 V at the glassy carbon electrode while passing the Hg(II) solution through the cell at 0.87 mL/min for 5 minutes. After this period, the potential was held at +0.05 V for 90 seconds. Following this conditioning, the stopcock was turned to stop the flow of mercuric ions and allow the flow of the deaerated sample solution through the cell. This flow was continued for 3 minutes to flush any mercuric ions from the system and replace all of the solution in the system with the sample to be measured. While the solution was flowing at a known flow rate (0.87 mL/min), the ASV deposition potential was applied to the thin-layer flow cell (usually for 1 minute) and the metal ions accumulated. At this point, the solution flow was stopped and after a 30 second equilibrium period, a potential ramp was initiated (-1.00 V to +0.20 V) and the stripping voltammogram recorded. The scan was terminated at +0.20 V. Solution flow was renewed and the electrode cleaned at +0.50 V for 90 seconds to prepare the system for the next determination. The mercury film was removed at the end of a series of experiments using a moist Kimwipe. The electrode was subsequently polished for the next series of studies.

RESULTS and DISCUSSION

The effectiveness of commercially available Reticulated Vitreous Carbon (RVC) was examined for its performance as the cathode material of the upstream metal removal cell. Minimal removal of ions was observed for the RVC via adsorption (no applied potential). Upon the application of a potential negative enough to reduce the metal ions, removal efficiencies of 10.2% and 50.0% were observed for Pb and Cd, respectively. In order to improve these efficiencies, several parameters must be addressed. By increasing the ratio of cathode surface area to electrolyte solution volume, increasing the time that the solution remains in the electrode material and/or by optimizing the potential applied to the cell, greater efficiencies can be obtained. This work examined the ability to improve removal efficiencies via greatly increasing the surface area either by altering the surface of the cathode material or by utilizing a proprietary high surface area carbonaceous material.

Two samples of the proprietary carbon material were received from an independent laboratory. Of the two, the more conductive and graphitic sample (Sample A) was used for analysis. The surface area of this material was measured to be 115 m^2/g. This surface area is 1000 times greater than that of the RVC. This large surface area should enhance the removal efficiencies of the working cell over those seen using planar cathodes or the RVC. The material was pretreated as described above. The pretreatment improved the wetting ability of the carbon surface and it also increased the measured surface area to 228 m^2/g. Good electrical contact was easily established between the carbonaceous cathode material and the platinum mesh lead. The ability of this material to remove cadmium and lead was addressed.

No effect was observed for the removal of the metal ions due to adsorption alone (i.e. no applied potential). Application of a negative potential greatly improved this material's ability to remove the metal ions. Figure 2 shows the effectiveness of this carbon material to remove cadmium and lead. The stripping voltammograms are shown for the metal ion solution (1) prior to being passed through the metal removal cell (FEED), (2) after the solution is passed through the cell with no applied potential (0.00 V) to assess adsorption and (3) after the solution was passed through the cell with an applied potential sufficient to reduce the metal ions at the cathode surface (-1.00 V). Minimal removal was observed due to adsorption. Efficiencies of 91% for cadmium and 95% for lead were obtained for the reductive removal of the metal ions. These large removal efficiencies show great promise for the use of high surface area carbonaceous materials for the cathodic removal of metal ions from aqueous streams.

A graphite fiber mat was assessed for it's ability to remove metal ions. Following the employment of the graphite mat to remove metal ions, the mat's surface was altered in a proprietary manner to increase the surface area. Prior to altering the surface, the mat had a surface area of 0.59 m^2/g. The surface area of the graphite fiber mat following alteration was 99.9 m^2/g. This was 167 times greater than that of the graphite fiber mats alone. The performance of the graphite fiber mats before and after alteration was assessed. The removal via adsorption alone resulted in the minimal removal of metal ions from solution. Upon the application of a sufficiently negative potential, improved removal was obtained. For the unaltered mat, virtually no removal was noted. However, when the altered mat was tested, removal efficiencies of 99%, 91% and 88% were accomplished respectively for Cu, Pb and Cd using an applied potential of -1.00 V. At a potential of -1.20 V, an effluent concentration of zero was measured for each of the metals.

A conductive graphite felt was analyzed in the next study. Both unaltered and altered graphite felt were utilized. Surface area measurements demonstrate the ability to increase the surface area by alteration. Prior to alteration, the surface area of the graphite felt was 0.17 m^2/g. Upon altering the surface, this was increased to 55.41 m^2/g, over a 300-fold increase. The performance of the bare graphite felt was first assessed. Minimal removal was seen due to adsorption. Upon applying a potential of -1.00 V, most of the lead (97%), but only 22% of the cadmium was removed. Solutions treated under the same conditions using the altered graphite felt removed the lead below detectable limits, as well as improved the removal of cadmium (46%). Application of a more negative potential and optimization of experimental parameters can be employed to improve these efficiencies.

To confirm minimal contribution from the platinum mesh, the system was tested in the absence of any carbonaceous cathode material. It was found that the platinum mesh does not contribute significantly (<2%) to the removal of the metal ions from solution.

Continuous removal of lead from an aqueous stream using electroplating on the proprietary carbon material was used to demonstrate the long-term effectiveness of the carbonaceous cathode. The lead solution was passed through the remediation cell and the ions were removed by applying the desired potential. A potential of -1.00 V was applied to remove lead via electroplating. Over a continuous period of 72 hours, a removal efficiency of 89% or greater was achieved for an inlet lead concentration of 100 ppm. Calculation of the lead removed over this period demonstrates a capacity of 0.90 g_{Pb}/g_{carbon}, but it should be stressed that even at 72 hours, the carbon showed no signs of saturation (see Figure 3).

The final desire is the recovery of the metals once they have been removed from the aqueous stream. It is possible to recover the metal ions plated onto the cathode surface simply by reversing the potential. This was demonstrated using a feed solution concentrated 100 ppm in lead ions. The lead ions were removed at a potential of -1.00 V for 3 hours. Subsequent recovery of the lead at a potential of +1.00 V produced an effluent stream more concentrated in lead. This concentration was 331 ppm lead, which demonstrated a 3:1 concentration of the waste stream. For mixed metal streams, individual metal ions can be selectively removed and recovered by these means.

A summary of the removal efficiencies for all of the carbonaceous cathodic materials is given in Table 2. As can be seen, some of these devices are extremely effective for the removal of heavy metal contaminants from aqueous streams.

CONCLUSION

The use of carbonaceous cathodes is an effective means to remove heavy metal contaminants from aqueous streams. By increasing the surface area of existing cathode materials or by using new high surface area materials, improvements in the removal efficiencies are obtained without the vast increase in the electrode volume. By careful selection of the appropriate experimental parameters, the selective removal and recovery of these metal ions is feasible.

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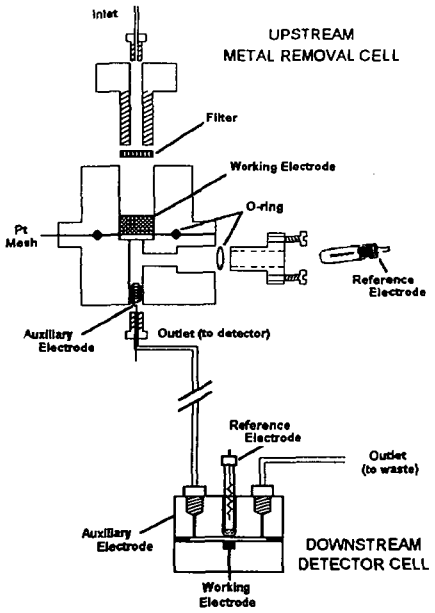

Figure 1: Schematic of Metal Removal Cell and Detector.

PROPERTIES of CARBON MATERIALS

Surface Areas

Material	Surface Area (m^2/gram)	
	BET	**Langmuir**
Proprietary Carbon Cathode		
Sample A	115.13 (227.8)*	186.78
Sample B	182.77 (192.3)*	286.03
Graphite Fiber Mats		
Untreated	0.59	-
Treated	99.92 (112.8)*	-
Graphite Felt		
Untreated	0.17	-
Treated	55.41	-
RVC		
100 ppi	0.092	-
80 ppi	44.80	-

Table 1: Surface Areas of the Various Carbonaceous Cathode Materials.

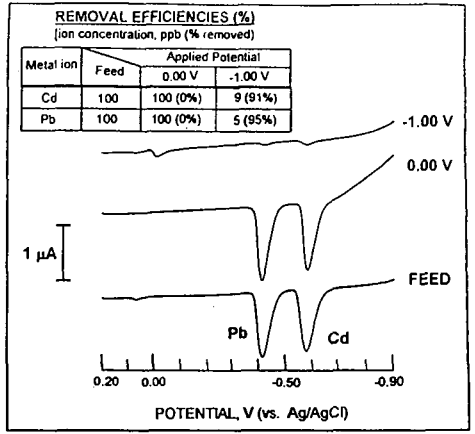

Figure 2: Metal ion Removal Using the Proprietary Carbon Cathode.

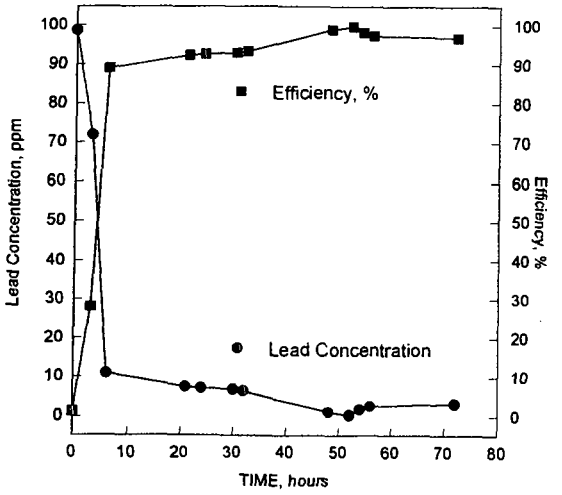

Figure 3: Long-term (72 hour) Removal of Lead via Electroplating.

TABLE OF REMOVAL EFFICIENCIES

Cathode Material	Cathode Potential, V	Metal Ion Removed Cd	Pb
RVC	0.00	16%	0%
	-1.00	50%	8%
Sample A	0.00	0%	0%
	-1.00	91%	95%
Untreated Graphite Mat	0.00	0%	0%
	-1.00	5%	17%
Treated Graphite Mat	0.00	0%	0%
	-1.00	90%	92%
Untreated Graphite Felt	0.00	13%	7%
	-1.00	22%	97%
Treated Graphite Felt	0.00	0%	0%
	-1.00	46%	99%
Platinum Mesh	0.00	0%	0%
	-1.00	0%	9%

Table 2: Removal Efficiencies of Various Carbon Cathodes.

ELIMINATION OF COPPER ION FROM ITS DILUTE AQUEOUS SOLUTION BY VARIOUS CARBON FIBERS UNDER APPLIED CATHODIC POTENTIALS

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Keywords: carbon fiber, waste water treatment, copper ion

SYNOPSIS
A series of carbon fibers were dipped in an acidic aqueous solution containing copper ion. Cathodic potentials were applied to them. Chronological variation of residual concentration was observed. The behavior was discussed based on electrochemical impedance spectrometry. The ultrahigh modulus carbon fiber performed the best under the condition most favorable for it. Poorly crystallized activated carbon fiber was not much behind. A carbon fiber with a high electro-conductivity and covered with prism planes of the graphitic layer over the surface would perform much better, if such a fiber were available.

INTRODUCTION

Elimination of copper ion from acidic waste water is a problem to be solved for manufacturers of print-circuit boards. The ion is eliminated by non-recycling processes or by recycling ones. Non-recycling ones are cheaper but dubious from environmental point of view. The reverse is the case for the recycling ones. This research is intended to develop a new, more economical recycling process on the basis of electrochemical deposition of the metal.

The material for the electrode for this purpose must be electro-conductive, chemically stable and of a large surface area. Carbon fibers are considered to satisfy these requirements to a reasonable extent. In order to specify the most appropriate fiber, we compared performance of a series of carbon fibers and discussed the behavior based on electrochemical impedance spectrometry (EIS).

EXPERIMENTAL

Employed carbon fibers are tabulated in Table 1. They cover fibers of a wide range of crystallinity, starting from a virtually-amorphous fiber from phenol resin, terminating at an ultrahigh modulus fiber (UHMF) from pitch. They include an activated carbon fiber from phenol-resin based carbon fiber (ACF). A wire of fine copper filaments was also used as a reference. This wire comprises 45 filaments of 170micrometers in diameter. Any fiber carries no coating and no sizing except for ACF, whose surface treatment in not disclosed.

Chronological variation of residual concentration of copper ion was observed with use of a cell depicted in Fig.1, together with details of the connecting section from the metallic terminal pipe to carbon fiber. The free length of the fiber was 40mm. Bottom 35mm of the fiber was dipped in a 15ml of 0.5M of sulfuric acid containing 124wppm of copper ion. A potential of -180mV or -100mV was applied to the terminal (as measured against an Ag/AgCl reference electrode. Also -200mV, 0mV and +100mV for ACF). Separate experiments were performed for each intended time of dipping. Neither mechanical stirring nor gas-bubbling was performed, because these actions might cause detachment of once-deposited metallic copper, which was weakly bonded to a fiber. Numbers of monofilament were approximately 3000 - 4500. Exact number varied depending on the specimen, because some fibers were in a form of yarn, and because their exact counting was not practical. Residual concentration was determined by an atomic absorption spectrum.

EIS was observed in an ordinary cell containing 500ml of the solution. The free length of the fiber was 25mm, and its bottom 5mm was dipped in the solution. The number of monofilament was approximately 2100 for ACF and 2000 for UHMF. Impedance was observed at in the frequency range between 100kHz through 100mHz at each increment of 0.2 of its logarithmic value. A bias voltage was selected from -200mV, -180mV, -100mV, 0mV and +100mV, as appropriate. Perturbation voltage was 10mV(0-p value). The impedance was calculated from integrated values of 1000cycles.

RESULTS AND DISCUSSION

Variation of the residual concentration

In the case of ACF, a nominal potential more cathodic than -100mV was required for elimination of copper ion. Variations of residual concentration of the ion at nominal potentials of -100mV and -180mV are illustrated in Fig. 2 for selected fibers. Tentatively the data are cited in as-observed values, not normalized by the surface area or another, because it is not certain what type of normalization makes sense. Amount of deposited metal varied along the fiber axis and/or among filaments. UHMF performed the best (whether normalized or not). But the other fibers, including those not shown here, were not much behind it.

The trends of the variation were almost identical for most of the cases. The variation in the first 12 hours (the initial period) was more or less different from what followed thereafter(the later period). The amount of the variation in the initial period varied considerably with fibers and applied potentials. For poorly-crystallized fibers it was almost always nil or a moderate decrease. For well-crystallized one, it was a drastic decrease at -180mV, while it was almost nil at -100mV. In the later period, logarithm of the residual concentration decreased almost linearly against time for most fibers, especially at -180mV. In the other words, the variations

were reasonably approximated with an equation of the type

$$\log(C) = p \cdot t + \log(q) \qquad (1)$$

C: residual concentration, t: time, p,q: constants.

This means that the rate of the elimination is roughly proportional to the residual concentration. The values of p were not much different among most of the fibers for a given potential. As the pattern of the variation was such that the performance of a fiber was controlled largely by the value of q, especially at −180mV.

A taper-off of the rate of the elimination or even an increase in the residual concentration was observed for certain high-performance fibers in a very later stage of their dipping. A likely cause for it is that some of excessively-grown metallic copper particles detached off the fiber and re-dissolved into the solution. They were found to be bonded to a fiber very weakly.

Electrochemical Impedance Spectrometry (EIS)

Shape of the Cole-Cole plots varied considerably from one fiber to another. Most of them were composed of two arcs, although some appeared to comprise a single arc or three arcs. Three cases of two fibers are discussed in this preprint.

Cole-Cole plots for ACF, one of the most poorly crystallized fibers, are shown in Fig.3. They are typical of two arc plots. They contain a large (apparent) solution resistance and two arcs, respectively of various sizes. The right arc, which is made from impedance seen in the lower frequency side (less than 1Hz) is understood to come solely from reaction(s) across the fiber/solution interface. The left arc, made from impedance in the region larger than 1kHz, is difficult to handle, because a signal of impedance was observed even when EIS was observed in air in this frequency range. It is understood to include impedance with the fiber.

Characteristic values of the right arcs of the plots shown in Fig.3 were evaluated by assuming an equivalent circuit shown in Fig. 4. R_{sol}, C_h & R_h, and C_l & R_l stand for (apparent) solution resistance, characteristic values for the left arc and those for the right one.

Results of the right arcs are shown in Fig. 5 (the values are based on the values of impedance observed at 0.25Hz). The values of charge transfer impedance are low. Both C_l and R_l decreased with time until a considerable amount of solid copper deposited on the fiber in the cases of the copper-containing solution, while only C_l decreased in the cases of copper-free solution. This implies deposited copper making an active center. The values of R_{sol}, R_h, R_l and their sum (which would be an approximate value of resistance when direct potential is applied) are summarized in Fig. 6. This chart reveals that a significant part of the total resistance goes to R_{sol}. The values of R_{sol} increased with time. Copper ion in solution diminishes R_h even when metallic copper does not deposit.

Fig. 7 illustrates Cole-Cole plots of UHMF, the most crystallized fiber, at a nominal potential of −100mV. Although they appeared to be composed of two arcs, they are of three. This is revealed from the plots of impedance against frequency (not shown). An arc at the high frequency end is too small to be seen in Fig. 7. This fiber shows a very small solution resistance. This chart includes plots for a copper wire observed when it was dipped in the same solution and in the copper-free sulfuric acid of the same molality. Although a chart like Fig. 5 or 6 cannot be prepared since the arcs are not well resolved, two facts are easily noticed. The first is that the initial impedance of UHMF in the copper containing solution is far higher than that of the copper wire. This means that UHMF is initially a semiconductor, if not an insulator. The second is that the shapes of the plots of UHMF approach with time to those of the copper wire in the copper-free solution.

Model of the Behavior of the Two Fibers.

ACF: Smaller value of R_l estimated from EIS for the fiber suggests that a large number of active sites are present over the fiber surface. That is an advantage of poorly crystallized fiber. That will be the reason why poorly-crystallized fibers perform not far behind the well-crystallized fibers. Most of high R_{sol} of poorly crystallized fibers is considered to emanate, not from genuine solution resistance, but from resistance of the carbon fiber, because it is much smaller for UHMF. This means that the potential difference across the fiber/solution interface is considerably lower than the nominal voltage applied by the potentiostat, (especially when current is large i.e. in the initial period), now that cathodic nature wanes along the fiber axis towards the free end of the fiber. This will be the reason why the performance is not so excellent in spite of the large number of active sites over the surface of this fiber. The larger values of R_{sol} result in a lower power efficiency.

UHMF: The initial high impedance across the fiber/solution interface of UHMF suggests that the surface acts initially as a capacitor. The large decrease in residual concentration seen in the initial period for this fiber at −180mV is likely due to enrichment of copper ion in or near the electrochemical double layer. The enrichment will be high, because the potential difference across the fiber/solution interface is large. The large potential difference over the whole interface is enabled by a low electric resistance along the fiber axis, which is evident from the low (apparent) solution resistance. This effect is small at a lower cathodic potential, say at −100mV.

After finishing the initial period, main mechanism of the elimination shifts from a capacitative nature to a depositing nature. Metallic copper will deposit and grow on the active sites, now possibly on the already-deposited copper particles. This will make the mechanism of the elimination more akin to that for the copper wire. This will be the reason why the EIS of UHMF approaches to that of copper wire (in the copper-free solution, because the solution

is diluted with time). The initial high impedance of UHMF suggests also that only a limited number of active sites are present over the surface. This is a disadvantage in terms of electric deposition. This will be the reason why UHNF performs not far ahead of the other fibers in the later period in spite of its high potential difference across the fiber/solution interface.

Conclusions

A pitch-based ultrahigh modulus (and some other high modulus) fiber performed better in the condition most favorable for it. But poorly crystallized (activated or ordinary) fiber performed not too bad. Their mechanisms appear to be based on different advantages. The advantage of the former group is their high electrical conductivity along the fiber axis. This makes whole surface evenly effective. Low electrical conductivity across their surface is advantageous in the initial stage at a deep cathodic potential, but it is rather disadvantageous otherwise, especially when the cathodic potential is shallow. Directions of the high and the low electrical conductivity are mutually replaced for the latter group. The low conductivity along the fiber axis and high conductivity across the surface are their disadvantage and advantage, respectively. It is likely that a carbon fiber with a high electrical conductivity covered by prism layers of graphitic layer over the surface would perform better than those examined in this work, when such a fiber is materialized.

Acknowledgement:
The authors acknowledge valuable contribution from Prof. Ohta, Prof.Toki, both of Yokohama National University, and Mr.Kuwagaki of Hokuetsu Tanso Co.

Table 1. Employed carbon fibers.

Code	In Fig.2	Manufacturer	Features
Activated C.F.	ACF	Toyo Boseki	Commercial product.
Ex-Kynol		Home-made	Virtually amorphous.
Ex-Kevlar		Home-made	Poorly crystallized, but oriented.
Ex-lignin	GLY	Nippon Chemicals	Poorly crystallized.
PAN High-strength		Toho-Rayon	Commercial grade.
PAN High-modulus	No.2	Toho-Rayon	Commercial grade.
Ex-Pitch 70ton	UHMF	Petca	Ultrahigh modulus, well-crystallized
Ex-pitch 50ton		Petca	High modulus, next to above.
Copper wire	Wire	-----	Commercial wire with vinyl cover.

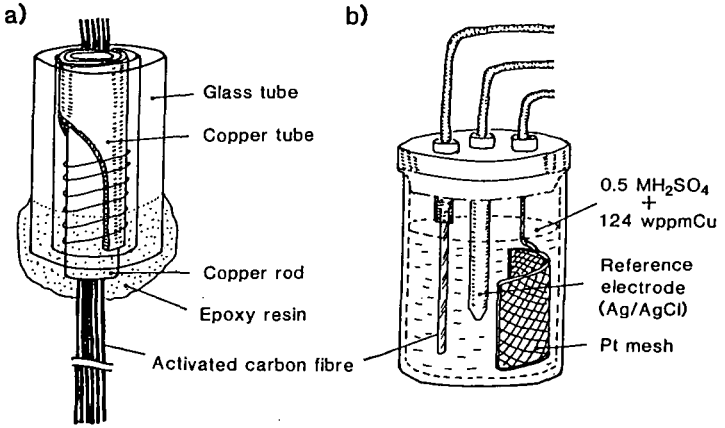


Fig. 1 Schematic illustration of the cell used for observation of residual concentration of copper ion.

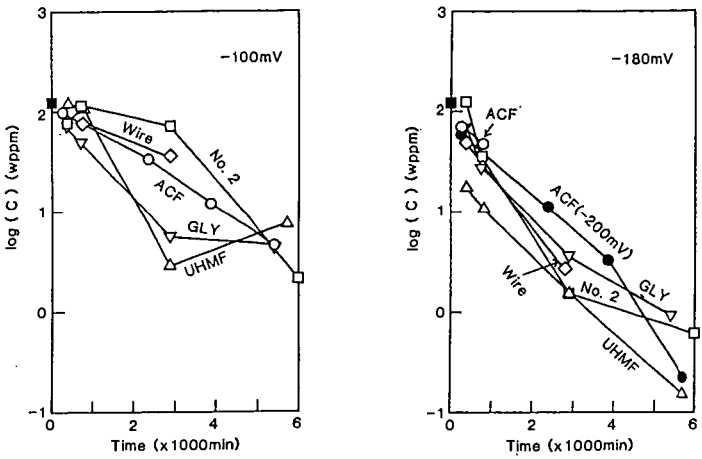


Fig. 2 Chronological variations of residual concentration of copper ion for ACF.

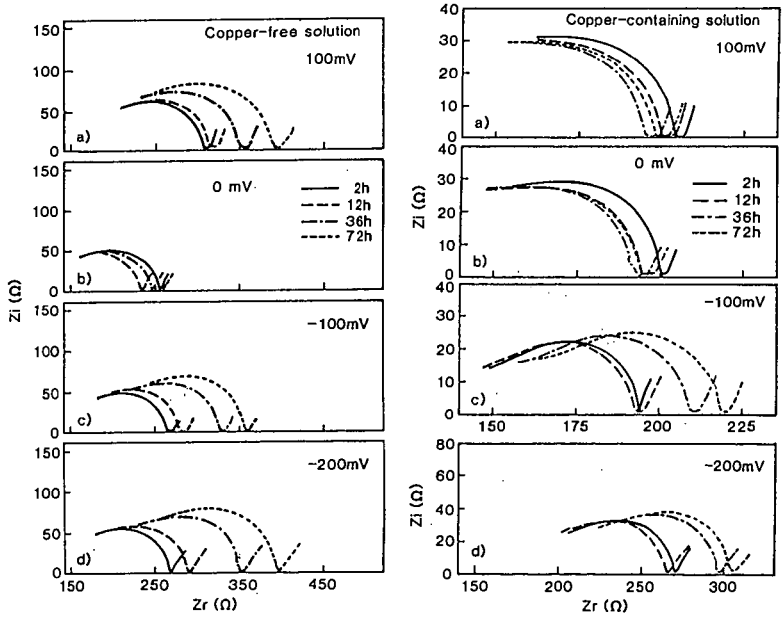
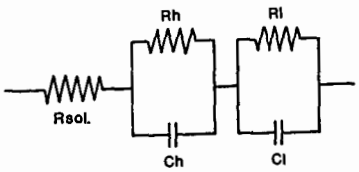


Fig. 3 EIS for ACF

Fig. 4 Equivalent circuit used for analysis of EIS of ACF



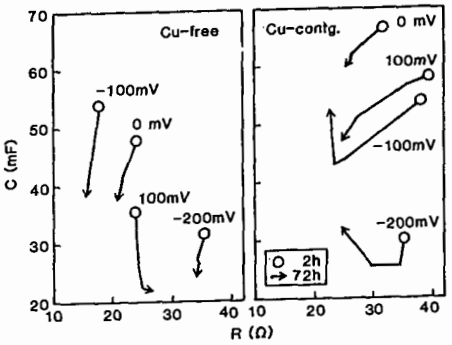


Fig. 5 Values of C_l and R_l for the right arcs shown in Fig. 3.

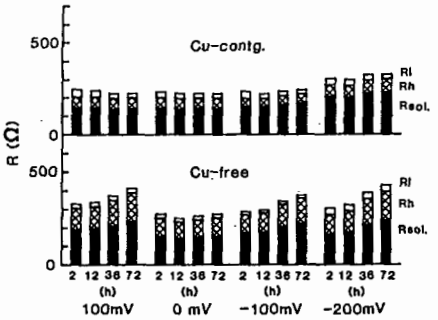


Fig. 6 Estimated contents of resistances under direct current for ACF

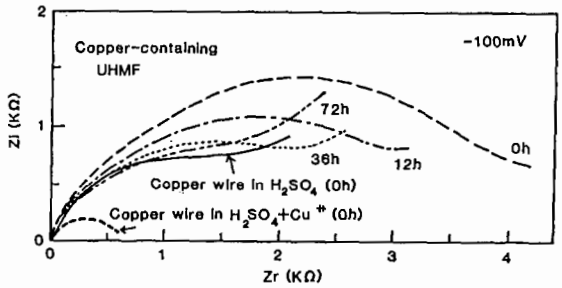


Fig. 7 Cole-Cole plots of UHMF together with those of copper wire.

CARBON BLACK AND CARBON BLACK-CONDUCTING POLYMER COMPOSITES FOR ENVIRONMENTAL APPLICATIONS

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Keywords: Pollutant, redox reaction, chromium.

INTRODUCTION

A large fraction of the carbon black commercially produced in the U. S. and other parts of the world goes into the automobile tire industry and other rubber applications. However, specialty applications of this material are expected to grow in the future. The present study explores the applicability of composites of carbon black and an electronically conductive polymer, polypyrrole, in environmental pollution abatement scenarios.

Chromium was used as a model environmental pollutant for demonstration of our approach. Chromium occurs in two common oxidation states in nature, Cr(III) and Cr(VI). Because it is only weakly sorbed onto inorganic surfaces, Cr(VI) is notoriously mobile in nature. On the other hand, Cr(III) is readily precipitated or sorbed on a variety of inorganic and organic surfaces at near neutral pH. The properties of Cr(III) and Cr(VI) have been reviewed with respect to acute and chronic toxicity, dermal toxicity, systemic toxicity, toxicokinetics, cytotoxicity, genotoxicity and carcinogenicity [1]. The hexavalent chromium compounds appear to be 10-100 times more toxic than their Cr(III) counterparts when both are administered by the oral route. The toxicology of chromium does not reside with the elemental form but varies greatly among a wide variety of many different chromium compounds. Oxidation state and solubility appear to be crucial factors in the regard [1]. Other aspects of chromium toxicity and carcinogenesis have been reviewed [2].

Reduction of Cr(VI) to Cr(III) followed by a pH adjustment to form the highly insoluble $Cr(OH)_3$ species would clearly be an effective means to counter the harmful effects of this element on the environment. It is worth noting that a wide variety of anthropogenic sources generate Cr(VI) in effluent streams: Chrome plating, electronic, metallurgical, timber, and leather tanning industries to name a few. Chemicals such as SO_2, $FeSO_4$ or sodium metabisulfite are currently used for Cr(VI) reduction. However, these chemicals are consumed in the process which also generates sludge and consequent solid waste handling problems.

We demonstrate herein a new electrochemical strategy for the environmental remediation of Cr(VI) that is based on *spontaneous* electron transfer to Cr(VI) from a pre-reduced conducting polymer (polypyrrole)-carbon black composite thus reducing Cr(VI) to the trivalent form. In doing so, the composite itself is oxidized, and can be *electrochemically recycled* back to the reduced state for a fresh treatment cycle. The present work builds upon an earlier effort [3] in these laboratories that utilized polypyrrole as the active material.

EXPERIMENTAL

The carbon black-polypyrrole composites and the parent conducting polymer were chemically synthesized. Polypyrrole was chemically synthesized from an aqueous 0.1 *M* pyrrole solution using potassium persulfate as the oxidant. Further details of the preparation procedure and characterization are contained elsewhere [4].

The polypyrrole-carbon black composite was prepared in a similar manner except that the polymerization medium contained in addition, the requisite amount of the N135 black [4]. Nominally, a composite containing ~43% (by wt.) of carbon black was utilized. In other experiments, the relative amount of polypyrrole and carbon black in the composite was varied by correspondingly varying the carbon black content of the polymerization medium [3]. For preparation of PVC-polypyrrole and PVC-carbon black composite, appropriate quantities of the two components were thoroughly mixed together (in a mortar and pestle) to afford ~43 wt.% of the active material (polypyrrole or carbon black). A similar procedure was also adopted in one instance for preparation of the polypyrrole-carbon black composite.

In all the experiments for this pilot study, pelletized rectangular-shaped samples were used. The pellet dimensions were chosen to fit inside a 1 cm path length quartz optical cuvette. The Cr(VI) solution comprised 1 *mM* of $K_2Cr_2O_7$ in 0.1 *M* H_2SO_4 yielding an initial concentration of Cr(VI) of 104 ppm. In a typical experiment, 2 *mL* of this solution were pipetted into the cuvette. Chromium (VI) has an optical absorption band at 350 nm that can be used to monitor its concentration. The optical absorbance of the solution in contact with the pelletized active material, was monitored at requisite time intervals after initial contact. All tests were performed at the laboratory ambient temperature.

The efficacy of the polypyrrole-carbon black composite for Cr(VI) reduction was compared against three reference samples: polypyrrole, and composites of polypyrrole or carbon black with an *inert* matrix polymer, namely polyvinylchloride (PVC). The carbon black used in this study (N135) was made by a furnace process.

RESULTS AND DISCUSSION

In a related study [3] we showed that spontaneous electron transfer occurs from an electrochemically pre-reduced polypyrrole sample to Cr(VI) consistent with a reaction scheme as follows:

$$Cr_2O_7^{2-} + 6\,PPy^0 + 14\,H^+ \rightarrow 2\,Cr^{3+} + 6\,PPy^+ + 7\,H_2O \qquad (1)$$

In the above equation, PPy denotes polypyrrole and the superscripts "0 " and "+" correspond to the reduced and oxidized states of the redox polymer respectively. Taking values for the standard reduction potential of –0.20V and +1.16V [3] respectively for the two redox couples in the above scheme, namely $PPy^{+/0}$ and $Cr^{6+/3+}$, the process represented by Reaction 1 has a standard free energy change of - 787 kJ/mol. One potential advantage of this approach (over currently-used chemical treatment schemes) is that the active material, polypyrrole, can be repeatedly shuttled back and forth between its two redox states (Figure 1). On the other hand, for a heterogeneous process (such as ours), very high surface dispersion of the active material obviously is desirable, and carbon black can serve this function as a "surface modifier" component. Figure 2 contains data showing the ability of chemically synthesized polypyrrole to reduce Cr(VI). Half of the original Cr(VI) is reduced after ~ 35 min. contact with polypyrrole as illustrated in Figure 2b. We presume (as verified by atomic absorption spectroscopy experiments in the previous case, Ref. 3) that most of the chromium resides in the solution phase as Cr(III). The solid line in Figure 2b is an exponential decay model fit to the data, consistent with first-order kinetics (see below).

Carbon black by itself can be compacted into a pellet; however it is much too fragile for routine handling and use in this form. Thus, PVC was chosen as an inert polymeric "binder." A pelletized sample of PVC alone gives no reduction of Cr(VI) during a 60 min. exposure. Next, a 40% (w/w) carbon black in PVC was prepared as described in the Experimental Section. The sample was first electrochemically pre-reduced (at –0.9 V, all potentials herein quoted with respect to Ag/AgCl reference) in 0.1 *M* H_2SO_4 prior to contact with the Cr(VI) solution; Figure 3 contains the results from this experiment. The lower Cr(VI) reduction rate in this case (relative to Figure 2) could be either a manifestation of the lower surface coverage of the active (carbon black) material, or an intrinsic difference between polypyrrole and carbon black. Nonetheless, the high activity of carbon black toward Cr(VI) was a bonus in terms of our new approach (see below). Again, the solid line in Figure 3b is an exponential decay model fit to the data.

Figure 4a contains data from an experiment wherein the potential of a carbon black-PVC composite electrode was continuously monitored during contact with Cr(VI). As before, the electrode was pre-reduced at –0.9V. On opening the circuit in 0.1 *M* H_2SO_4, the electrode potential gradually relaxes to the "rest" value. When the solution is subsequently dosed with Cr(VI), the potential undergoes a sharp excursion in the positive direction prior to attainment of a plateau. This excursion is symptomatic of the oxidation of the electrode surface by Cr(VI).

In order to examine whether the oxidation resulted in introducing oxygen functionalities at the carbon black surface, XPS spectra of the carbon black samples were compared before and after Cr(VI). No change in the C1s binding energy was noted. The lack of adsorption of chromium onto carbon black was also signaled by the absence of the chromium peaks at 44 eV (3 p), 576 eV (2 $p_{3/2}$) and 586 eV (2 $p_{1/2}$) in the XPS data. Similarly, experiments on samples before and after Cr(VI) contact show no significant change in Lc and La from the initial values of 11.10 Å and 23.50 Å, indicating that the material removal (by oxidation) occurs without alteration of the carbon black crystallite size within the matrix.

The driving force for electron transfer from carbon black to Cr(VI) can be tuned by controlling the potential of the former. This is shown in Figure 4b wherein three types of samples, namely a "neutral" (electrochemically untreated) specimen, a sample pre-oxidized at +0.9 V and one pre-reduced at –0.9 V, are compared in terms of their relative efficacy for Cr(VI) reduction. Electrochemical reduction raises the electron energy levels in the carbon black whilst the corresponding electronic states in the untreated and oxidized samples lie at lower energy levels. Stated in alternative terms, the reduction capacity of carbon black can be electrochemically tuned.

The PVC-carbon black composite exhibits classical electronic percolation behavior [21]. That is, there is a critical carbon black concentration in the matrix at which particle connectivity is established. Beyond this threshold (which occurs at ~ 20% (w/w) of the black), rapid increase in the electronic conductivity occurs with further carbon black loading, quickly obtaining a plateau [4]. Figure 5 contains Cr(VI) conversion data for four different PVC-carbon black samples. Samples containing carbon black at levels below the percolation threshold exhibit negligible activity toward Cr(VI). Interestingly, there is an abrupt increase in the activity at the threshold beyond which only a modest increment occurs for the 40% (w/w) black PVC-carbon black sample.

Figure 6 contains a comparison of the relative efficacy of polypyrrole and carbon black for Cr(VI) reduction. These data were generated on three types of samples: a polypyrrole-carbon black composite, a reduced PVC-carbon black composite and a polypyrrole-PVC composite. The polypyrrole-carbon black composite contained ~ 43% (w/w) of carbon black. To facilitate the

comparison, all these samples were "diluted" to the same extent with the PVC binder to afford 40% (w/w) of the active material. That is, the polypyrrole-carbon black composite in this particular experiment had a composition of 22.8% (w/w) polypyrrole, 17.2% (w/w) carbon black and 60% PVC in the final pelletized sample.

Interestingly, the composite containing *both* polypyrrole and carbon black as the active material exhibits the highest activity for Cr(VI) reduction. Further, carbon black (at least the grade used in this study) outperforms polypyrrole in its ability to reduce Cr(VI). The conversion data in Figure 7 can be fitted to a pseudo first-order kinetics scheme.

The influence of carbon black level in the polypyrrole-carbon black composite on the ability of the latter to reduce Cr(VI) was also considered. Contrary to the experiments considered earlier in Figure 6, the composite samples in this case were prepared *without* the PVC binder. A systematic improvement in the composite performance is noted with an increase in the carbon black content although the rate of improvement tends to saturate at the higher loadings.

SUMMARY

This study has shown that the composites outperform both polypyrrole and carbon black in terms of their ability to reduce Cr(VI). It is worth nothing that in the composite, both redox (polypyrrole) and oxidizable (carbon black) functions are built into the material framework. The former is reversible and the latter is irreversible. This is fortuitous in an economic sense in that carbon black is the less expensive of the two components, and can be periodically replenished. The stability of polypyrrole in repeat use cycles was also briefly explored in this study. No appreciable and systematic loss of conversion efficiency was noted over three Cr(VI) conversion cycles as long *as the electrochemical regeneration (reduction) step was essentially complete.* This latter process is a function of the polypyrrole morphology and the reduction potential used, and could encompass a time period anywhere from a few seconds to a few minutes. In our hands, a regeneration potential of –0.9 V in 0.1 *M* H_2SO_4 and a reduction time of 30 minutes were effective in restoring the activity of the sample.

We have used compacted samples for the active material in this study, merely for experimental convenience. A practical Cr(VI) treatment system can be envisioned to consist of a *packed bed* through which the effluent stream could be recirculated. This bed would comprise fine (μm size) particles of the polypyrrole-carbon black composite. Electrical contacts could be introduced via procedures routinely adopted for packed-bed electrochemical flow reactors (c.f. Ref. 5). Ideally, the charge-transfer kinetics at the active material/solution interface must be fast enough such that the system is under mass-transport control. Further efforts will focus on optimizing the Cr(VI) conversion kinetics at the polypyrrole-carbon black particle/solution interface. The fact that the reaction half-life is independent of the initial Cr(VI) concentration is encouraging in this regard.

A practical system would also require a pH adjustment step to immobilize the reduced Cr(III) onto the sample bed. The immobilized $Cr(OH)_3$ could be reoxidized and released in a subsequent back-flushing cycle so that the Cr(VI) treatment system also regenerates Cr(VI) for fresh reuse. Further development of our Cr(VI) pollution abatement approach and the implementation of a practical system along the lines outlined in the previous paragraphs, are continuing in these laboratories.

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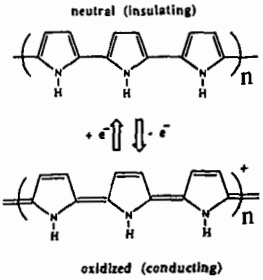

Figure 1. Neutral and oxidized redox states of polypyrrole and their inter-convertible nature.

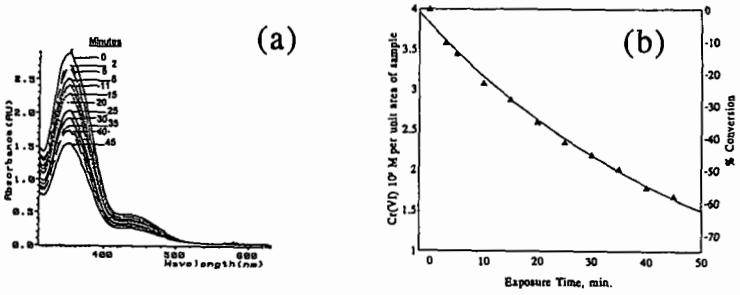

Figure 2.

Data illustrating the ability of chemically synthesized polypyrrole to reduce Cr(VI). UV-VIS spectra are shown in Figure 2a, and the Cr(VI) conversion *vs.* time computed from these spectral data are contained in Figure 2b. The numbers on the spectra in Figure 2a show the contact time with Cr(VI). The initial Cr(VI) solution composition is specified in the Experimental Section. The solid line in Figure 2b is a least-squares fit of the data (see text).

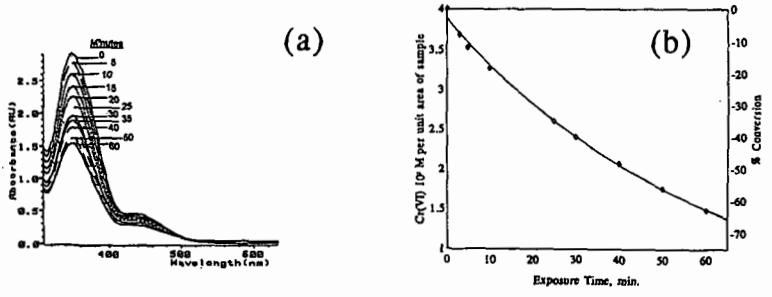

Figure 3.

Data illustrating the ability of carbon black to reduce Cr(VI). UV-VIS spectra are shown in Figure 3a, and the Cr(VI) conversion *vs.* time computed from these spectral data are contained in Figure 3b. The spectral notation in Figure 3a as in Figure 2a. The carbon black was dispersed in PVC to yield a composite containing 40% (w/w) of the black. The sample was first reduced at –0.9 V in 0.1 *M* H_2SO_4 prior to Cr(VI) contact.

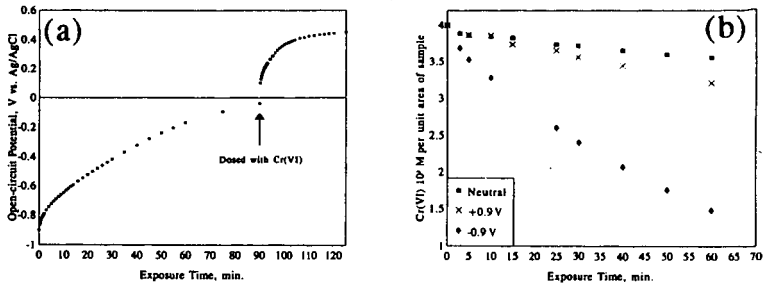

Figure 4. (a) Variation of the open-circuit potential of a PVC-carbon black composite electrode (30% w/w of carbon black) before and after contact with the Cr(VI) solution. The electrode was pre-reduced at -0.9V in 0.1 *M* H_2SO_4 prior to opening the circuit and monitoring the potential. (b) Effect of electrochemical pre-treatment (in 0.1 *M* H_2SO_4) on the ability of a PVC-carbon black composite (30% w/w of carbon black) to reduce Cr(VI).

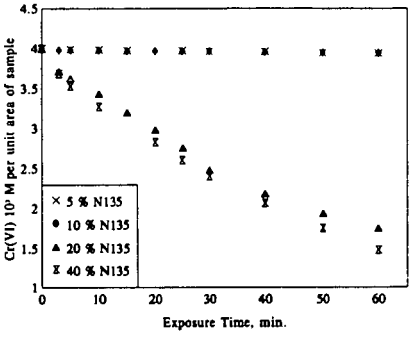

Figure 5. Influence of carbon black level (in the PVC-carbon black composite) on the Cr(VI) reduction ability of the composite. The percolation threshold in the composite occurs at ~20% (w/w) of the black (refer to text).

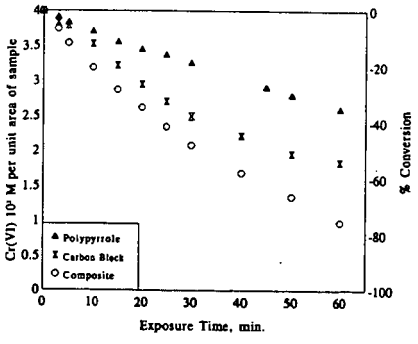

Figure 6. Comparison of the relative efficacy of polypyrrole, carbon black and the polypyrrole-carbon black composite for Cr(VI) remediation. The composite contained ~43% (w/w) of the black. In all the three cases, the active material was diluted to 40% by mixing with the inert PVC (refer to text).

DESULFURIZATION STUDY OF HYDROCARBON MOLECULES BY PLASMA PROCESS FOR GASOIL APPLICATIONS

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Keywords: thermal plasma, fluidized bed, desulfurization

ABSTRACT

During these last years, many investigations have been made on sulphur elimination processes from hydrocarbon feedstocks because of environmental regulations which are more and more strict. This is a study on a plasma process dedicated to heavy hydrocarbon hydrotreatment and hazardous substances removing such as sulphur compounds. It is a co-processing of a fluidized spouted bed and an inductively coupled plasma working at atmospheric pressure. A high flow of hydrogen radicals is generated and a rapid quench of the plasma leads to an increase of hydrogen radical life-time and promotes chemical reactions of desulfurization at low temperature (700-900 K).
The primary objective of this work is to understand the cleavage of C-S bond under these plasma conditions. To this end, thermodynamic calculations are done and preliminary experiments are carried out with different mixtures where n-hexadecane is chosen as the model molecule in hydrocarbon hydrocracking, and sulphur compounds are added in small amounts (0-1 % S wt). Compounds such as dimethyl sulphide, 2-butanethiol, benzothiophene and thiophene are currently studied. The influence of $CH_3°$, H°, HS° and PhS° ($C_6H_5S°$) is also considered.

INTRODUCTION

The development of upgrading processes in order to convert heavy feeds to lower boiling products, have to take into account the presence of components which make processing difficult, such as sulphur compounds. Besides, one of the operational problems of upgrading heavy feeds is the formation of undesirable high amounts of coke, which represent losses in hydrocarbonaceous materials and also need a costly separation step [1].
The development of such processes requires improvement of certain properties, especially H/C ratio. This is equivalent to adding hydrogen or rejecting carbon. For this reason, considerable attention is given to hydrogen addition technologies (hydrocraking) as opposed to carbon rejection technologies (thermal processes).
It has been revealed that hydrogen plays an important role in the activation and control of conversion of heavy feeds into marketable products [2,3]. However, high conversion of heavy feeds into distillate products require an efficient hydrogen activation, which can be promoted by adding a suitable catalysts. Nowadays many new and hydrotreatment catalysts are entering the market and their evaluation in terms of activity and stability is the subject of many recent works [4]. However, their use presents also inconvenients which are mainly reliable to deactivation phenomenon - due to the coke deposition and sintering of the active sites [5,6] - and also to the high cost of the active metal species.
Our approach in this paper is to present briefly a new upgrading thermal inductively coupled plasma process working under atmospheric pressure and dedicated to heavy hydrocarbon hydrocracking. The plasma produces a high flow of hydrogen radicals and a spouted bed is used for the plasma quenching in order to avoid coke formation. The coupling of the plasma and the spouted bed provides a non equilibrium system where hydrogen radicals amounts are 1000 times greater than those in an equilibrium system [7]. The use of such a process seems to be suitable since the high temperature and the high flow of radicals provide high efficiency of molecule decomposition such as sulphur compounds. In fact, plasma may operate by providing a source of hydrogen radicals through the dissociation of molecular hydrogen and then these radicals can promote the bond cleavage reactions.
Since many years, investigations have been made on sulphur compound addition effects on various hydrocarbons such as methane [8], propane [9], heptane, n-nonane [10], and in petroleum fractions such as naphtha [11]. Sulphur compounds, like thiophenics have long been known to be fairly stable thermally and relatively unreactive. At this end, the behaviours of compounds such as thiophene, in n-hexadecane is investigated in this paper. The studies are also directed towards extending these experiments to industrial feed stocks like gas oil. The analytical results are obtained by off-line gas chromatography.
Moreover, the reactor parameters have to be taken into account, so as to point out the properties of the plasma phase (H° and $CH_3°$ radicals) and those of the solid phase (Al_2O_3, CaO, $CaCO_3$).
In the same aim, a preliminary and predictive study had been realized on C-H-S-O system, and thermodynamic calculations permitted to determine the gas phase evolution: the stable species versus the temperature, the pressure and the initial composition of the gas mixture, and then optimal reactor parameters.

PREDICTIVE CALCULATIONS

Thermodynamic evolution of the gas phase. Thermodynamic calculations for C-H-S-O system give information about stable species in function of temperature, pressure and initial composition of the gas mixture. Moreover, these calculations lead to the prediction of optimal reactor parameters towards the distribution of molecules in the gas phase at the equilibrium state.
The principle of calculations is based on the Gibbs free energy minimization of the studied mixture using a second order Taylor method [12].

The calculation parameters are:
— thermodynamic parameters: pressure, temperature and free enthalpy versus temperature,
— different species considered at the equilibrium (molecules, atoms, ions, radicals),
— initial composition of the chemical mixture. Thermochemical data are taken from Janaf tables [13].
The computational program can only consider homogeneous phase cases. So, phenomena involved in solid phase interaction could not be taken into account. Besides, this method does not predict the kinetic evolution of the physicochemical system.
In order to study the desulfurization of sulphur containing hydrocarbons, a first simulation was made, it is intended to represent the decomposition of an average petroleum section ($C/H/O/S = 1/1.4383.10^{-3}/3.10^{-3}/1.7.10^{-2}$) [14]. This result shows the important role of temperature and initial composition in C-S bond cleavage.
The major products obtained (fig.1) are light hydrocarbons (CH_4, C_2H_2..), aromatic hydrocarbons (C_6H_6), and sulphide molecules such as H_2S and CS_2. We observed that the effect of hydrogen addition (fig.2) is to eliminate progressively sulphur from hydrocarbon chains by formation of hydrogen sulphide which can easily be trapped by inert solids. The decomposition of sulphide hydrocarbons must be carried out at temperatures under 2000 K, because of the growth of their stability with temperature elevation. Besides, the increase of oxygen amount in those systems leads to the apparition of toxic molecules such as SO_2, CSO and CO (fig.3).

Thermodynamic study of the heterogeneous phase. One of the main objectives of this study in using a solid phase in the plasma post-discharge is to keep toxic molecules level in gas effluents under the ppm value. The toxic elements such as H_2S can be eliminated from the gas phase by trapping on solid particles and producing an inert solid [15]. The possibility of using alkaline earth oxides in such heterogeneous systems was demonstrated by means of free energy diagram of sulphur compounds (fig.4). This diagram represents the thermodynamical stability of solids versus temperature and it suggests that using a spouted bed of alkaline earth oxide, like calcium oxide, seems to be suitable for trapping toxic sulphur containing gas by calcium sulphide formation. These can be possible at temperature up to 1170 K where calcium dioxide is able to react with toxic gases.

EXPERIMENTS AND RESULTS

Experimental equipment. The reactor (fig. 5) is composed of a double-flow inductively coupled plasma torch made of quartz and working with an argon-hydrogen mixture. The inductor is made of four water cooled copper coils. The double flow torch, supplied with up to 20% hydrogen in argon, is injected laterally in a two dimension spouted bed reactor. The inductively coupled plasma (5.4 MHz, 18 kW) is characterized by a global efficiency of 50%. The bed is a parallelepipedical refractory reactor with a regime of a jet spouted bed [16], where particles - Al_2O_3, $CaCO_3$ or CaO, (250-350 μm) - are fluidized by argon or hydrogen. The formed particle fountain divided the bed in two parts :
— the region in front of the plasma with temperatures in the range of 2500-1800 K,
— and the region behind the fountain with temperatures in the range of 700-1100 K.
The hydrocarbon feedstocks are injected in the latter region.

Hydrocracking experiments. The decomposition of n-hexadecane was investigated in the presence and absence of sulphur compounds which are introduced into the reaction system together with the feed. The purpose of this work is to study the influence of dimethyl sulphide, 2-butanethiol and methyl-phenyl sulphide on the conversion rate of n-hexadecane and on yields of products. Hydrogen sulphide produced is measured for each experiment by way of tube gas (Prolabo). The bed particles used are alumina particles (350 μm). All sulphur compounds are added in the mixture at the same content: 1 % wt of sulphur, in order to achieve comparable experiments. The hydrocarbon composition of gaseous and liquid product mixtures was determined by gas chromatography.
The qualitative and quantitative composition of the sulphur products are still not possible at this time for analytical problems, nevertheless their effects on n-hexadecane decomposition are observed.
Gaseous products are analysed by gas chromatography (Girdel 30, flame ionization) with ST104 column, and liquid ones by Shimadzu GC-9A chromatographe (flame ionization) with an SE 30 non polar column. Carbon black quantification is done thanks to reflectance measurements on normalized filters.

Mass balance and conversion rate. The mass balance is realized for gases and liquids. Analysis lead to mass balance in term of conversion as follows:
Conversion C (% mass) = mass flow n-C_{16} initial/mass flow n-C_{16} after reaction
Two samples are taken on the effluent gas: one in a glass gas sampling bulb (for gases C_1-C_4) and an other one in a liquid nitrogen trap (for liquid compounds C_5-C_{16}) (fig.5).

Experimental conditions. Pressure: 1 atm, power : 4.16 kW, plasmagen gases: argon and hydrogen : 27l/min and 3l/min respectively, fluidization gas: argon: 42.9 l/min, total hydrocarbon flow: 0.4 kg/h, particles used: alumina 350 μm.

Hydrocracking of n-hexadecane. Previous works on n-hexadecane hydropyrolysis in plasma spouted bed reactor at atmospheric pressure and realized in the laboratory are summarized in the following conclusions:

— linear light α–olefins are principally obtained where ethylene and propylene are the major products,
— the carbon black formation can be neglected,

— the residence time is very short about 0.3 seconds,
— n-hexadecane conversion rate increases while hydrogen flow increases,
— hydrogen radicals produced by the plasma and quenched by the fluidized bed are involved in radical reaction processes, especially in initiation ones.
Under these conditions, at 973 K, with a residence time of 0.3 second, the cracking yield obtained is 37.4 % (wt). The major products are ethylene (33.45 %), propylene (11.81 %) and CH_4 (6.8 %). Olefins represents about 90 % (wt) of the cracking products, and the coke less than 0.5 % (wt).

Effects of sulphur compounds on n-hexadecane hydrocracking. The addition of sulphur compounds leads to an increase of gas and n-hexadecane conversion rate (table 1). Experimental conditions are on the whole similar, except for the fourth experiment (Me-Ph-sulphide) where the temperature is higher and the process is more a thermal one, but on the whole the conversion rate increase by 8 % for thiophene addition, 18 % for dimethyl sulphide and 2-butanethiol. The hydrocarbon product (without sulphurs) distribution is not really affected in these operating conditions in terms of quality, nevertheless, an increase of olefins of 2 % is observed (fig.6). Besides, C_2H_4 and C_2H_2 decrease while an increase of C_4H_6 can be noted.
Hydrogen sulphide amount for thiophene mixture is the lowest one (5 ppm) because this compound is thermally stable and relatively unreactive. These properties have been attributed to its conjugated structure which allows the free electron to be largely delocalized. The highest value is for 2-butanethiol mixture (140 ppm), and for sulphides : dimethylsulphide and methyl-phenyl sulphide, hydrogen sulphide emission is at about the same.
These results suggest that under plasma conditions, the cleavage of hydrocarbons is intimately related to the appearence of highly reactive light radicals such as $CH_3°$, H°, HS° and PhS° and which influence the course of radical reactions and the rate of hydrogen transfer is one of the main factors to be considered in mechanism understanding. Thus, the fact that thiols have the ability of accelerating H-transfer reaction by a factor of 200 [17] might be explain at least in part the increase of n-hexadecane conversion for 2-butanethiol mixture.

Cracking of gas oil feedstock. The behaviour of a classical industrial feedstock (<150-450°C>; S = 1.5 % wt) has been studied in the plasma spouted bed reactor. This oil product was characterized before and after the treatment (fig. 7).
The effect of this treatment is to reduce heavy hydrocarbons (>300°C) from 60 to 18 %, while conserving the middle product (<150-300°C>) up to 40 %.
Sulphur compounds of the considered petroleum fraction have also been analyzed before and after plasma treatment [18] on SPB sulfur column (Supelco) with chemiluminescence detector. The preliminary observations were the followings:
— presence of sulphur compounds in the gas-oil : aliphatics and cyclics,
— hydrogen sulphur emission during plasma treatment, testifying to C-S bond cleavage,
— reduction of mercaptans and sulphides amounts,
— dealkylation of substituted benzothiophene,
— thiophene production after treatment which is testimony to ring opening.
Alkylated sulphur compounds in gasoline feedstock are sources of $CH_3°$ radicals which have an effective influence on reactions occurring during hydrocarbon plasma pyrolysis. This is validated by the increasing of the conversion rate in case of aliphatic hydrocarbons such as n-hexadecane.

CONCLUSION

Sulphur compounds under plasma conditions, introduced into the reaction system together with the feed, catalyses the rate of n-hexadecane decomposition and influence the selectivity especially in terms of coke precursors during hydropyrolysis. Compared to the pure n-hexadecane, the decomposition rate increases by 8 to 18% depending on the nature of added sulphur compounds which are effective H-transfer catalysts and improve the yield of α-olefins. The decomposition increase as the amount of thiyl radicals is increased. In case of gas oil feedstock, a dealkylation of substituted sulphur compounds and ring opening in aromatic ones are observed

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Compounds added to n-hexadecane (1%S wt)	T_b (K) (bed temperature)	T_{inj} (K) (injector temperature)	% Gases	Conversion rate (%)	Hydrogen sulfur (ppm)
n-hexadecane	973	483	62	37.4	0
Thiophene	993	803	58	45.2	5
(Me)2S	993	803	67	55.3	60
2-Butanethiol	1028	872	79	55.4	140
Me-Ph-S	1123	871	88	84.3	65

Table 1: sulfur compound effects

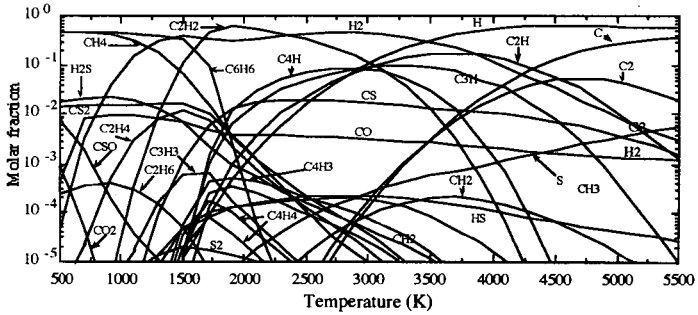


Figure 1: Complex Equilibrium of the system: C:H:O:S = 1 : 1.438 : 3.10^{-3} : $1.7.10^{-2}$ at P=1atm.

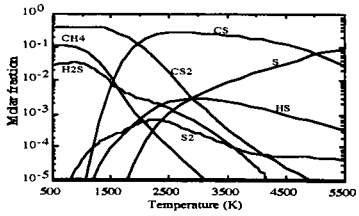


Figure 2: Complex equilibrium of the system: C:H:S = 4 : 4 :1, at P=1atm

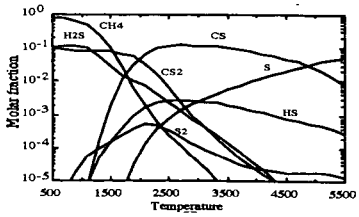


Figure 3: Complex equilibrium of the system: C:H:S = 4 : 12 : 1, at P=1atm

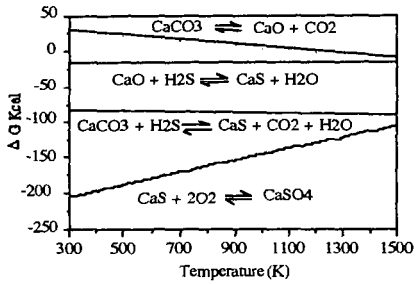


Figure 4: Free energy of different heterogeneous reactions versus temperature

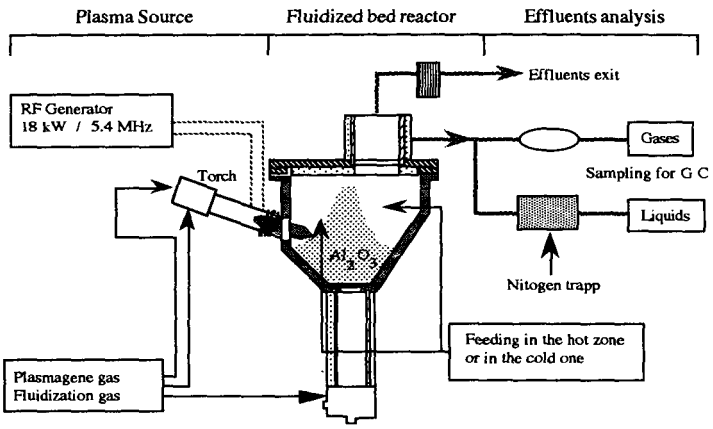
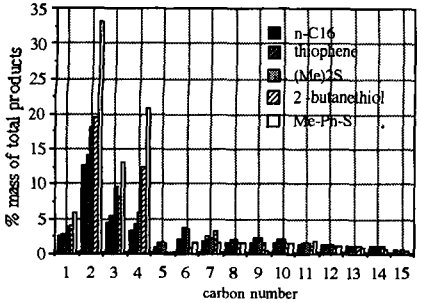


Figure 5 : General flow sheet of the plasma fluidized bed reactor



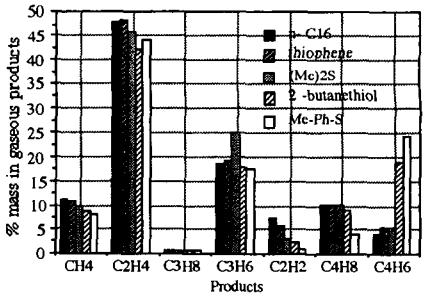
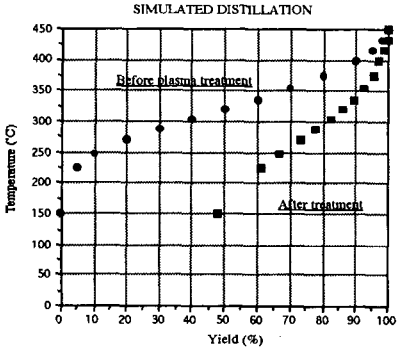


Figure 6: Products distribution for different mixtures with n-hexadecane (1% S



Experimental parameters :
Pressure: 1 atm
Plasma : Ar_{axial} = 15 l/min, Ar_{tg} = 12 l/min, $H2_{tg}$ = 3 l/min, Fluidization: Ar = 39 l/min
Power : 4.16 kW
Particles : Al_2O_3 :450 g , Ø= 350 μm
Feedstock: Gas oil (S=1.5 % wt), flow : 384 g/h
Residence time : 0.3 sec, temperature: 740 °C

Figure 7 : Results of gasoline hydropyrolysis